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British Association for the Advancement of Science

Reports on colloid chemistry and its general industrial application.

Vol.3. Third report. 1919.

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Department of Scientific and Industrial Research.

British Association for the Advancement of Science.

Reports on colloid chemistry

# THIRD REPORT

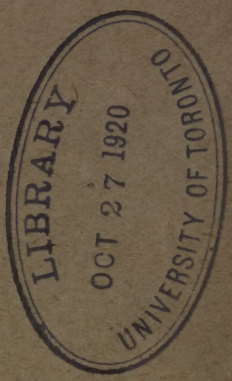
1919

ON

# COLLOID CHEMISTRY

AND ITS

# GENERAL AND INDUSTRIAL APPLICATIONS.




LONDON:
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1920.

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The First Report of this Committee was issued in 1917 by the British Association, Burlington House, London, W.1, from whose Office copies can be obtained, price 2*s*. It contains sections on the Viscosity of Colloids, and on Tanning, Dyeing, Fermentation Industries, Rubber, Starch, Gums, Albumin, Gelatine and Gluten, Cements, Nitrocellulose Explosives, Celluloid, and Physiological and Biochemical subjects.

The Second Report was published on behalf of the Department of Scientific and Industrial Research by H.M. Stationery Office, from whom copies can be obtained price 1*s*. 6*d*. net, or 1*s*. 8½*d*. post free, at any of the addresses named below. It contains sections on Peptisation and Precipitation, Emulsions, the Liesegang Phenomenon, Electrical Endosmose, Colloids in various industries, and Colloid Chemistry in Physiology.

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(*See also page 3 of cover.*)

Department of Scientific and Industrial Research.

British Association for the Advancement of Science.

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## PREFATORY NOTE.

At the request of the British Association for the Advancement of Science, the Department of Scientific and Industrial Research have decided to extend to the Third Report on Colloid Chemistry and its General and Industrial Applications the arrangements made last year under which the Second Report was published for the Department by H.M. Stationery Office.

The Third Report gives an account of the work accomplished during the year 1919 by the Committee of the Chemical Section of the British Association. As in the case of the previous volumes in this series, the preparation of the present Report has been entirely the work of the Committee of the Association, who assume full responsibility for all statements of opinion or of fact contained therein. The share of the Department of Scientific and Industrial Research in the work is limited to arranging for publication of the Report in order to ensure that the information contained therein, which it is hoped will prove valuable, may quickly be made available.

Department of Scientific and Industrial Research,
16 and 18, Old Queen Street,
Westminster, S.W.1.

*September*, 1920.

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*Colloid Chemistry and its General and Industrial Applications.—Third Report of the Committee consisting of* Professor F. G. Donnan (*Chairman*), Professor W. C. McC. Lewis (*Secretary*), Dr. E. Ardern,* Dr. E. F. Armstrong, Professor W. M. Bayliss and the late Professor A. J. Brown, Mr. W. Clayton,* Dr. C. H. Desch, Mr. W. Harrison, Mr. E. Hatschek, Professors H. R. Proctor and W. Ramsden, Dr. E. J. Russell, Mr. A. B. Searle,* Dr. S. A. Shorter, Dr. H. P. Stevens, and Mr. H. B. Stocks.

## Introduction.

The plan already adopted in the two previous Reports of arranging the subject matter under two heads, viz. : (1) classification according to scientific subject; and (2) classification according to industrial process, has been employed in the present Report.

The subjects dealt with under the first head in the accompanying Report are :—

1. Colloid Chemistry of Soap, Part I.—Solutions. By Professor J. W. McBain.
2. Ultramicroscopy. By G. King, M.Sc., F.I.C.
3. Solubility of Gases in Colloidal Solutions. By G. King, M.Sc., F.I.C.
4. Electrical Charge on Colloids. By J. A. Wilson.
5. Imbibition of Gels, Part I. By J. A. Wilson.

The subjects dealt with under the second head are :—

6. Imbibition of Gels, Part II.—Industrial Applications. By J. A. Wilson.
7. Colloid Problems in Bread-Making. By R. Whymper.
8. Colloid Chemistry in Photography. By Dr. R. E. Slade.
9. Collodion in Photography. By H. W. Greenwood.
10. Cellulose Esters. By Foster Sproxton, B.Sc., F.I.C.
11. Colloid Chemistry of Petroleum. By Dr. A. E. Dunstan.
12. Asphalt. By Clifford Richardson, M.Am.Soc., C.E., F.C.S.
13. Varnishes, Paints, and Pigments. By Dr. R. S. Morrell.
14. Clays and Clay Products. By A. B. Searle.

The Committee has again to express its sense of obligation to the authors of the sections enumerated above.

A number of subjects yet remain to be considered. It is hoped that these will be dealt with in the Fourth Report.

W. C. McC. Lewis.

* Names so marked are those of Assessors or Consultative Members, not being Members of the Association.

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# COLLOIDAL CHEMISTRY OF SOAP.

## PART I.—SOLUTIONS.

*By* J. W. McBain, *Leverhulme, Professor of Physical Chemistry, University of Bristol.*

### I.—*Brief Résumé.*

Recent investigations of aqueous soap solutions culminating in 1914, have revealed soaps as a prototype of a great class of colloids remarkable alike for their theoretical interest and their industrial importance. The substances belonging to this class have been defined by McBain and Salmon[14] as " colloidal electrolytes."

Colloidal electrolytes are salts in which one of the ions has been replaced by a heavily charged, heavily hydrated ionic micelle which exhibits equivalent conductivity that is not only comparable with that of a true ion but may even amount to several times that of the simple ions from which it has been derived. In other words, this ionic micelle is a typical but very highly charged colloidal particle of very great conductivity.

The conductivity of such a colloidal electrolyte is quite comparable with that of an ordinary electrolyte. On the other hand since the ionic micelle exhibits only the osmotic effect characteristic of an ordinary colloid, the total osmotic activity of the colloidal electrolyte is correspondingly deficient and may be distinctly less than that of a non-electrolyte. Thus high conductivity goes hand in hand with only moderate osmotic effects.

Some of the very numerous substances which must be recognised as belonging to this group are the protein and gelatine salts (T. Brailsford Robertson's well-known alternative hypothesis, which is to the effect that there are no ordinary ions present, but that the protein salts ionise into two colloidal ions resembling ordinary slow complex ions, appears to have been built up upon early E.M.F. data which Pauli, Manabe, and Matuli have since shown to be erroneous), dyes, such as Congo-red, indicators, the higher sulphonic acids and hydrochlorides, tellurates and many inorganic substances; in fact, most substances of high molecular weight or containing long carbon chains which are capable of splitting off an ordinary ion.

The soaps are a particularly interesting case for investigation in that their chemical formulæ are well ascertained, tautomerism does not occur, true reversible reproducible equilibrium is established in all solutions, and finally the definite transition from typical simple electrolyte through colloidal electrolyte to neutral colloid may be observed in all its stages. This transition from crystalloid to colloid is exhibited not only in passing from salts of the lower to those of the higher fatty acids, but may be demonstrated in any one of the higher members merely upon change of temperature and concentration.

This striking and wholly unexpected combination of properties on the part of the ionic micelle, was plausibly explained in 1913 by the writer, on mechanical grounds. This conception is based upon the consideration of the application of the principle contained in

Stokes' Law, that the frictional resistance to motion of a definite amount of substance depends directly upon its degree of subdivision. Thus, if say ten simple palmitate ions unite to form one single particle carrying ten electrical charges, the resistance to movement under the action of the electric current is considerably diminished and therefore one should expect greatly enhanced conductivity. This is, indeed, observed to a very appreciable extent in some cases, but it is partly off-set by the action of this enormous aggregation of electrical charges in condensing upon the particle large amounts of water and, indeed, any other constituent available in the solution such, for example, as undissociated colloidal soap. This also obviated the difficulties advanced by Bayliss[19] in proposing his tentative assumption of a mere aggregation of the anions of Congo-red.

This heavy hydration is held by many authorities to be a plausible explanation of the high viscosity frequently exhibited by substances of this class as well as the effect of varying conditions upon this viscosity, and it also accounts for the effects of temperature, for example, the high temperature coefficient of the conductivity.

The recognition of this class of colloid in spite of the assistance of isolated data for particular cases, was long delayed owing to the supposed irreconcilability of these properties and to their being ascribed to the presence of impurities and hydrolysis, &c. It will be seen that the results have now been experimentally established beyond reasonable doubt.

It is worth while noting that a colloidal electrolyte differs wholly in its behaviour from the class of substances represented by the dextrines which may be termed "semi-colloids." The semi-colloids are non-electrolytes exhibiting various degrees of osmotic activity, ranging from that of a typical crystalloid such as dextrose down to that of a colloid such as starch.

It is also worth while mentioning that cataphoresis has often been confused with conductivity. Most ions and charged colloidal particles and even coarse suspensions exhibit a velocity of cataphoresis of the same order of magnitude, but it is only in the case of the ions and a few selected cases of colloids that this has been regarded as being identical with conductivity. In dealing with colloids, in no case was a conductivity predicated greater than might be expected for a very slow-moving complex ion, whereas the theory of the ionic micelle predicts enhanced conductivity, and in the case of soap experiment shows that ionic micelle has to be recognised as being several times more mobile than the ions from which it is derived.

The writer incidentally considers that it has not yet been proven that there is any difference in kind between cataphoresis and ionic migration, except that in an ion the number of electrical charges is equal to the number of equivalents of substance in the ion. If so, electrical endosmosis would be a result of solvation. Quantitative data are being sought in order to test this point.

### II.—*Constitution in Alcohol.*

In alcohol soaps exhibit a wholly different and much simpler behaviour. The soap here exists in the form of a simple unpolymerised

electrolyte in true solution, whereas in most aqueous solutions it is of course a colloidal electrolyte. The conductivity is only moderate, and the ebullioscopic measurement indicates that it is a rather weak electrolyte.

The great dissimilarity in the constitution of soaps in alcohol and aqueous solution is brought out strikingly in an observation of the writer. When alcohol is added to a clear aqueous solution of sodium oleate the oleate is immediately salted out as a transparent gel, although this readily dissolves again after a few minutes shaking.

There are, however, colloidal properties in alcoholic soaps which require further investigation. Thus, although Miss Laing[12] has proven that in solutions of potassium oleate in dry alcohol at boiling point there is no appreciable proportion of colloid present, yet sodium oleate solutions, which have not yet been carefully studied in anhydrous alcohol, are said to solidify to a gel on cooling; and this would appear to prove the presence of a large amount of colloid. Potassium oleate on the other hand solidifies to a white curd on cooling. Oleic acid itself in all concentrations of alcohol is a simple electrolyte only very slightly dissociated.

## III.—*Hydrolysis, Hydrolysis-Alkalinity and Products of Hydrolysis.*

### (a) *Hydrolysis-Alkalinity.*

Until quite recently, the extent of the degree of hydrolysis and the hydrolysis-alkalinity of soap solutions has been a moot point, the estimates ranging practically from neutrality up to nearly complete hydrolysis. This was due to the difficulty of finding a satisfactory method of investigation, one which should not destroy the soap solutions that were being subjected to measurement.

The two methods introduced by McBain and Martin[24] and McBain and Bolam[25], that of E.M.F. and rate of catalysis have sufficed to establish that the alkalinity of soap solutions is very small, being of the order of magnitude of 0·001 N free OH′ for most concentrations of soap. The E.M.F. method is of doubtful application where unsaturated compounds are present, as in the case of all commercial soaps, and the catalytic method is only applicable in dilute solutions at high temperatures.

The hydrolysis-alkalinity of soap solutions depends upon the concentration, the temperatures, the nature of the soap, and upon its state of aggregation.

Taking first the effect of concentration; in extreme dilution hydrolysis is very appreciable, but once the concentration of soap approaches decinormal, the hydroxyl ion increases but slowly with future increase of concentration and passes through a flat maximum shortly before normal concentration is obtained.

The results obtained by E.M.F. in sodium and potassium soaps at 90° are given in the following table in which all concentrations are expressed in weight normality. Diffusion potential was not taken into account; a recalculation in which diffusion potential is allowed

for gives appreciably lower values for the alkalinity of the more concentrated solutions :—

| Soap. | Sodium Palmitate. | | Potassium Palmitate. | |
|---|---|---|---|---|
| | OH′ | % Hydrolysis. | OH′. | % Hydrolysis. |
| 1·0 N - | 0·0020 | 0·20 | 0·0008 | 0·08 |
| 0·75 N - | 0·0023 | 0·30 | 0·0024 | 0·31 |
| 0·5 N - | 0·0019 | 0·37 | 0·0032 | 0·65 |
| 0·1 N - | 0·0013 | 1·28 | 0·0013 | 1·25 |
| 0·05 N - | 0·0011 | 2·22 | 0·0010 | 2·02 |
| 0·02 N - | — | — | 0·0011 | 5·6 |
| 0·01 - | 0·0007 | 6·6 | 0·0007 | 6·8 |

The hydrolysis of soap solutions above decinormal (3 per cent. soap solution) is only a fraction of 1 per cent., and it is not very different for sodium and potassium salts. The falling off in alkalinity in concentrated solution is probably quite real, the chief experimental error is in the opposite direction and the diminishing alkalinity is readily accounted for by the disappearance of the hydrolysable palmitate ion to form ionic micelle. The addition of sodium chloride also diminished the alkalinity, which in this case, however, passes through a minimum, since whenever a soap solution becomes heterogeneous, its alkalinity becomes distinctly increased. Further measurments show that the soap solution persists in being distinctly alkaline, even in presence of large excess of palmitic acid. Thus an excess of 10 per cent. palmitic acid reduces the alkalinity to two-fifths of that given in the table, and even in presence of 100 per cent. excess of palmitic acid the OH′ is still 0·00004 N. It is very important to note that even this slight degree of alkalinity precludes the existence of more than minute traces of free fatty acid in any soap solution, so that any solid product of hydrolysis can never be free fatty acid, but must always be an acid soap, intermediate in composition between neutral soap and $NaHP_2$, where P represents the fatty acid radical.

It is equally important to note that when the excess of alkali is added, it is not appreciably taken up by the soap present but remains almost entirely in the free condition, in other words, basic salts are not formed.

If various fatty acids are compared it is found that degree of hydrolysis increases rapidly as the homologous series is ascended.

Influence of temperature again is important. The hydrolysis-alkalinity decreases with lowering of temperature as, indeed, would have been expected.

Very few measurements of the hydrolysis-alkalinity of commercial soaps have been made, but the OH′ concentrations of solutions made from soaps which were finished neutral, are usually less than that of sodium palmitate.

(*b*) *Degree of Hydrolysis.*

Whilst the experimentally determined values of the hydrolysis alkalinity, that is, the concentration of hydroxyl ions, seems to be well established, it is a matter of opinion how to interpret these in

terms of hydrolysis. The writer regards the extent of hydrolysis as being identical with observed alkalinity, in this particular case, as in most cases. Bancroft, however, in the Second Report (1919, p. 15) has expressed his opinion that soaps are really greatly hydrolysed, but that the hydroxyl ion is almost completely adsorbed by undissociated sodium palmitate. Not to mention the difficulty in accounting for the disposal of the equivalent quantities of palmitic acid set free, this interpretation is diametrically opposed to experimental data, which show that any excess of hydroxyl ion added to a soap solution, remains free in the solution as such and is not adsorbed.

(*c*) *Products of Hydrolysis.*

Since all soap solutions are slightly alkaline, they must contain at least small amounts of products of hydrolysis. This has been observed from the time of Chevreul, who found that most soap solutions exhibit fine suspensions of acid soap of varying composition, varying between nearly neutral soap and a soap in which the alkali is deficient by any value up to one-third of the theoretical value for a neutral soap. The more dilute the solution, as Krafft and Stern[17] have found, the more nearly the composition of the suspensions approaches that of a sodium hydrogen soap ($NaHP_2$). McBain, Laing and Taylor find that acid soap formed in palmitate solutions at 90° has the composition HP.2NaP.

Whereas in aqueous solution even the presence of one complete equivalent excess of palmitic acid still leaves free OH′ present, a concentration 40 times as great as that required for coloration of phenol phthalein, the alkali is so rapidly diminished by the addition of alcohol that titration can be carried out in 40 per cent. ethyl alcohol, although 60 or 80 per cent. solution is distinctly preferable.

(*d*) *Effect of Carbon Dioxide.*

Although the dissociation constants of the fatty acids are perhaps 40 times greater than that of carbonic acid, yet the comparative insolubility of the fatty acids and of the acid soaps often results in extensive decomposition of the soap by excess of carbon dioxide. Even alcoholic solutions are decomposed. As a rule, the result of the interaction is the visible separation of acid soaps, as Krafft,[17] Stern,[17] and Wiglow[17], and Fendler[22], and Kuhn[22] showed. In the case of soaps from such oils as olive oil, however, the solution remains clear. Repeated treatment with carbon dioxide removed progressively less of the fatty acid, although ultimately nearly all may be removed. The equilibria involved have not as yet received quantitative study.

The solubility of the fatty acids is slight, nevertheless they are sufficiently strong to make it impossible for them to exist even in such concentrations in the presence of more than the merest traces of alkali hydroxide. The theoretical necessity for the existence of minute traces of free acid in all soap solutions is substantiated by the observation of Krafft and Wiglow, that soap solutions yield appreciable concentrations of fatty acid when shaken out with toluene or petroleum

ether, solvents in which the concentration of a fully saturated solution would be very great. The fact that such extracts are far from saturation—concentration is further proof that the fatty acid in the aqueous layer cannot have reached its minute saturation value either.

### IV.—*Evidence for, and Properties of, the Ionic Micelle.*

(a) *Conductivity.*

Soaps particularly in concentrated solutions all exhibit a high conductivity quite comparable with that of, say, sodium acetate. This conductivity must be a property of the soap, since as we have seen, there is very little free alkali present, and there is nothing else to which the conductivity can be ascribed. These points are well brought out in the following table from McBain and Martin's paper, which comprises the conductivity of sodium and potassium palmitate solutions divided in each case into their two components; that due to free hydroxide as indicated above and the remainder of the observed conductivity which has to be ascribed to the soap itself. The ratios of the conductivity of the soap to that of the corresponding acetate solutions are also given for comparison :—

| Cone. | Sodium Palmitate. | | | Potassium Palmitate. | | |
|---|---|---|---|---|---|---|
| | $\mu$ NaOH | $\mu$ NaP. | NaP/NaAc. | $\mu$ KOH. | $\mu$ KP. | KP/KAc. |
| 1·0 N | - 1·10 | 83·6 | 0·644 | 0·46 | 123·7 | 0·699 |
| 0·75 N | - 1·65 | 85·8 | 0·619 | 1·87 | 126·0 | 0·685 |
| 0·5 N | - 2·1 | 87·4 | 0·568 | 3·8 | 123·2 | 0·627 |
| 0·3 N | - 2·7 | 84·3 | 0·499 | — | — | — |
| 0·2 N | - 3·0 | 79·4 | 0·444 | 3·8 | 107·2 | 0·492 |
| 0·1 N | - 7·0 | 75·5 | 0·387 | 7·5 | 99·5 | 0·421 |
| 0·05 N | - 12·2 | 76·4 | 0·368 | 12·1 | 98·7 | 0·396 |
| 0·02 N | - — | — | — | 33·5 | 99·7 | 0·380 |
| 0·01 N | - 36·0 | 101·7 | 0·446 | 40·6 | 131·0 | 0·435 |

The form of the conductivity curve is remarkable, and is such as has hitherto been observed only for certain anomalous non-aqueous solutions. Both relatively and absolutely, the conductivity is at a minimum between 0·05 N and 0·1 N solution. Thereafter, instead of decreasing steadily with increasing concentration, the conductivity rises to a pronounced maximum in 0·75 N solution. The relative conductivity as compared with the corresponding acetate, has nearly doubled with this same increase of concentration. These unique relationships clearly establish that when such soap solutions increase in concentration, the palmitate ion is being replaced by some other, much better conductor of electricity, namely, the ionic micelle already referred to.

The experimental evidence for the reliability of these results rests upon a very painstaking study carried out during several years by McBain and Taylor,[2] in which all possible sources of error were carefully studied and eliminated in the special case of sodium palmitate.

This was necessary in order to place beyond controversy the fact that colloids could exhibit a proper conductivity that could not be explained away as being due to unknown impurities in accordance with universal custom hitherto. There has since accumulated a mass of corroborative evidence in the measurements carried out by Taylor,[2] Cornish,[3] Bowden,[4] Bunbury,[4] Martin,[8] and Laing[12] in collaboration with the writer; as also the measurements carried out by F. Goldsmidt and his co-workers,[6] Weissman[7] and Kurzman,[9] and by Reychler,[5] and by Arndt and Schiff.[10] (*See* the classified list of references appended.)

When the results for the potassium and sodium salts of all saturated fatty acids from acetic to behenic acid and likewise the oleates, are reviewed, the utmost regularity is observed in the gradual and regular transition from a typical curve of an electrolyte presented by sodium acetate through the appreciable deviations of the lower fatty acids (hexoates and caprate) to the laurate, in which a step out or maximum and minimum is first observed (in the case of sodium and potassium laurate respectively).

It must be borne in mind that some of these solutions are extremely viscous whilst others are quite fluid. This enormous alteration in viscosity appears to exert no effect upon the conductivity. Work at present being carried out by Miss Laing in collaboration with the writer shows that when the soap solution has been converted into a solid gel, its conductivity, vapour pressure and concentration of sodium ions are identical with that of the same solution in a state of fluid sol at the same temperature and concentration. This revolutionary observation appears to us to be of great importance for the theory of gels since here the constituent out of which the mechanical structure of the gel is built up has to be recognised as constituting one of the best conductors present or the colloidal ionic micelle has to move as freely through the stiff colloidal gel (where structural constituent must then be neutral soap) as through the fluid sol itself. This work and the conclusions to which it leads will be reported upon elsewhere.

The independence between conductivity and viscosity is further exemplified by the temperature coefficient of conductivity. In some cases the viscosity is diminished several hundred fold by rise of temperature and yet the temperature coefficient of conductivity is no greater than in others where the viscosity is not so markedly affected. The fact that the temperature coefficient is rather higher than that of an ordinary typical electrolyte is ascribed to hydration and hence increased mobility of the ionic micelle with rise of temperature.

Finally it should be noted that although potassium and sodium soaps exhibit a surprisingly close general resemblance, the typical relationships which have been described are rather more markedly exhibited by the solutions of potassium soaps which evidently contain rather greater quantities of ionic micelle.

(b) *Osmotic Pressure.*

It is, perhaps, hardly realised how difficult it is to obtain really reliable and unambiguous determinations of the osmotic activities

of colloids. The well-known osmometer method in which the membrane is not always strictly semipermeable involves a further very serious and not completely evaluated complication described in Donnan's approximate theory of membrane equilibria. Results of such measurements therefore are almost always subject to a certain ambiguity of interpretations. The classical methods of boiling point, lowering of vapour pressure, and freezing point lead to results which are beyond question, only provided that the essential conditions for the application of these methods are fulfilled.

The classical experiments of Krafft and of Smits using boiling point and vapour pressure respectively were completely vitiated by the unsuspectedly large amounts of dissolved air from which soap solutions cannot readily be freed and which develop a partial pressure quite comparable with the lowering of the vapour pressure of an ordinary crystalloid or electrolyte. To carry out a single vapour pressure measurement really requires several weeks of effort. The result then obtained is in agreement with those by the dew point method, to be described below. The osnometer data of Moore and Parker,[16] in the case of soaps were wholly erroneous on account of the effects of carbon dioxide.

The effect of dissolved air can be completely eliminated and accurate measurements of the vapour pressure made, by a modification of the dew-point method described by McBain and Salmon.

The freezing point method is applicable where solutions remain in sol condition at the freezing point and where ice separates out in crystals free from colloid. In the case of soap solutions the latter condition was attainable by inoculation, but very few soap solutions are liquid at 0° C. Determinations of all these have been published by McBain, Laing, and Titley.[13]

Thus the bulk of the available data for soap solutions are those obtained by the dew-point method which possesses an additional advantage in that it can be utilised at any temperature.

The results of the lowering of dew-point and freezing point agree in establishing the fact that soap solutions have a very real osmotic pressure of the same order of magnitude as that of a non-electrolyte such as sucrose. A continuous series of values for the osmotic activity is obtained, depending upon the concentration and position in the homologous series, which range from a fraction of that for non-dissociated crystalloid to that of a moderately dissociated electrolyte.

In discussing osmotic data, it is almost always essential to keep clearly in view the very important effect which hydration exerts in magnifying the apparent osmotic pressure more especially in concentrated solution. For instance, the apparent dissociation of electrolytes frequently exceeds 100 per cent. according to osmotic methods.

It is generally agreed that hydration is greatest at lower temperatures. In the case of the potassium salts of the lower fatty acids this enhanced osmotic effect is clearly visible at 0° as compared with the more normal results at 90°, but in spite of the magnification of osmotic data at lower temperatures the osmotic activity exhibited by soap

is very decidedly less at 0° than at 90°. Soap solutions are very much more colloidal at lower temperatures than at the boiling point, and the presence of colloid extends into comparatively dilute solutions at 0°.

In case of the higher soaps the relative osmotic activity is practically independent of the concentrations above 0·4 N at 0°, showing how complete the formation of colloid has been. Again, potassium octoate is distinctive in its behavoiur at 0° in that in lower concentrations it is a typical electrolyte whereas in extreme concentrations the relative osmotic activity rapidly diminishes.

(c) *Concentration and Composition of the Ionic Micelle.*

The evidence for the existence of the ionic micelle is based primarily upon comparison of conductivity and osmotic data. Briefly it amounts to this, that in concentrated solution of the higher soaps, the osmotic activity is often only about one half that required to explain the conductivity. The conductivity is, say, 2/3 of that of a salt like the acetate, whereas the osmotic pressure is, say, half that of a non-electrolyte such as sucrose, and yet both sets of data are fully trustworthy. The osmotic activity, therefore, corresponds with that of one ion only, and the other half of the current must be carried by an ion that is colloidal so as not to exhibit appreciable osmotic activity, and that nevertheless retains the sum total of the electrical charges of the ions from which it was derived. This is the ionic micelle.

The osmotic activity measures the total concentration of crystalloidal matter of all kinds. The conductivity measures the $K \cdot$ or $Na \cdot$ in addition to the carrier of the equivalent negative charges. To reconcile the experimental data, say in normal solution of potassium laurate at 0°, it is necessary to ascribe the whole of the observed osmotic activity to the potassium ion, and even when this is done, about half of the conductivity is still to be accounted for and must then necessarily be ascribed to colloid. It is notable that the equivalent conductivity thus ascribed to the ionic micelle of potassium laurate is about three times greater than the sum total of the conductivity which the separate laurate ions that are grouped in the micelle, would have exhibited if they had retained an independent existence. This, however, as the writer has indicated above, is only what would have been predicted from Stokes' Law, since the resistance offered to a particle increases directly with its diameter. When a number of small particles coalesce to form larger particles, the diameter of the larger particle does not increase by any means in the same ratio, whereas the electrical driving force will be directly proportional to the number of aggregated laurate ions if these latter have retained their equivalent electrical charges. Therefore for electrical forces the mobility of such a large particle is very great, whereas its diffusibility is only that of a colloid.

It is necessary to make some sort of assumption as to the mobility of the ionic micelle for a particular case in order to be able to evaluate the conductivity observed. A safe provisional rule is to ascribe to the ionic micelle, the minimum conductance which will serve to

reconcile the conductivity and osmotic effects. Of course, when it is possible to take hydration into account as it is hoped to do when certain measurements have been completed, the equivalent conductivity of the ionic micelle will then be ascertained.

On reviewing the results for all concentrations and temperatures, it is found necessary in concentrated solutions to ascribe to the ionic micelle a conductance which is equal to that of the potassium ion. This is by no means identical with the well-known and striking fact that the mobility of many mechanical suspensions as well as of colloids in the electric field is as great as that of an ordinary ion, since in the case of the ionic micelle of soap it is not merely the mobility but the equivalent conductivity that is so great.

There is a good deal of evidence for the conception that the mobility of the ionic micelle increases with concentration owing to diminishing hydration due to increasing amount of neutral colloid in the micelle. The most important considerations is, that otherwise it would follow from the principle of mass action that within a very narrow range of concentration the colloidal electrolyte would pass completely into undissociated form and no longer conduct.

The small but unmistakable difference between a potassium and a sodium palmitate solution is not readily accounted for if the ionic micelle is considered to be merely an aggregate of palmitate ions, and, therefore, necessarily identical in the two cases. There are a number of reasons for considering that the ionic micelle contains some of the colloidal undissociated sodium and potassium palmitates respectively, which would thus account for the difference in behaviour, since thus the micelles are no longer identical.

For these reasons the formula ascribed to the ionic micelle in a soap such as sodium palmitate is—

$$(\mathrm{NaP})x\cdot\ (\mathrm{P}')n\ \cdot(\mathrm{H_2O})m.$$

According to this formula, the composition of the micelle must alter continuously with change in concentration or temperature or upon the addition of salts. Thus in very concentrated solution or in presence of large amounts of another electrolyte such as sodium hydroxide or chloride, the soap must be nearly all colloid of approximately the composition—

$$(\mathrm{NaP})x\cdot\ (\mathrm{P}')n\cdot\ \ (\mathrm{H_2O})m.$$

Again this formula accounts for the real difference, namely, in conductivity and osmotic behaviour, between solutions of potassium and sodium soaps, as was pointed out above.

With regard to the value of n, the number of negative charges on the micelle, it must be at least 10, and probably is very much greater. Thus the " molecular weight " of the ionic micelle must be at least of the order of magnitude of 3,000, although the true molecular weight of palmitate is only 255. In a similar way the enormous molecular weights ascribed to various substances which occur only in the colloidal form may well be derived from the aggregation of comparatively small molecules.

One solution may be cited to illustrate typical values of the concentrations arrived at for the respective constituents 0·6 N KOl at 0° — 18°, is found to contain 0·17 N potassium ion, not more than 0·01 of other crystalloidal matter, the remainder being entirely colloid, probably largely included in the ionic micelle and comprising 0·16—0·17 N aggregated oleate ion, with a total of 0·41—0·43 N aggregated neutral potassium oleate.

In many other cases, however, the limits of concentration of the constituents have not yet been so narrowly defined.

## V.—*Physical Properties of Soap Solutions.*

Having discussed the general constitution of soap solutions, we shall now discuss in turn a number of their chief physical properties.

(a) *Viscosity.* (For references, *see* classified bibliography appended.)

As in the case of so many colloids the viscosity constitutes a prominent characteristic responding in typical fashion to alteration in experimental conditions. Whilst very readily measured and reproducible, the data do not lend themselves to quantitative interpretation and explanation. Nearly all our exact knowledge of this subject is due to the numerous and careful measurements of F. Goldschmidt[6] [7] and his collaborators, although Farrow carried out a series of exact measurements at 70° in Donnan's laboratory.

The viscosity increases with rise in concentration of the soap, at first gradually, then enormously. For instance, potassium oleate at 20° exhibits a viscosity of 1·19 for N/20, 1·87 for N/5, 8·02 for 0·4 N, and no less than 1573 for 0·6N, taking water as unity.

The effect of temperature in the case of less viscous soap solutions is practically that of the alteration of the fluidity of water.

Addition of hydroxide, chloride or carbonate at first lowers the viscosity, which passes through a minimum, and thereafter rises enormously. This was observed by Mayer, Schaeffer and Terroine,[26] Botazzi and Victorov[27] and Leimdörfer, Farrow,[28] Goldschmidt and Weissmann, and most carefully studied by Kurzmann.[9] The more concentrated the soap solutions, the more pronounced is the minimum, and the less the salt required to produce it.

The following data present typical cases of such minima produced by the addition of potassium hydroxide at 20° and at 90° to solution of 0·375 N, potassium laurate and 0·6 N potassium oleate respectively, the viscosity of water at 20° being taken as unity :—

At 20° the viscosity of the laurate is decreased from 1·96 to 1·57, that is, by 20 per cent. At 90° the decrease is from 0·604 to 0·522, being 14 per cent. At 20° the values for the oleate are 1573 to 728, by 54 per cent. At 90°, 3·80 to 3·01 by 21 per cent. These remarkable changes are produced by the addition of 0·5 N KOH to the laurate, but only 0·02N KOH to the oleate.

It is at once apparent that the lowering of the viscosity is dependent upon the presence of ionic micelle. There must be at least three primary effects at work in all these cases. The first, lowering is

dehydration through lowering of the reactivity (vapour pressure) of the water upon addition of the salt and its ions; for as McBain and Salmon have indicated, the heavily hydrated micelle must be extraordinarily responsive to such slight changes in the availability of the water. The second factor is formation of ionic micelle through the influence of the added potassium ion. The third, like the second, raises the viscosity, and consists in that unexplained change which, upon further addition of salt, tends to produce a jelly perhaps ten thousand times as viscous in the original soap. This last effect may well be due to the formation of neutral undissociated colloid and its subsequent linking up as explained in Section VI below. It is interesting to note that in accordance with all these views such high viscosities are more quickly obtained by adding further quantities of the soap itself, rather than by adding equivalent amounts of salt or alkali.

However, it must be concluded that the foregoing is merely a programme or working hypothesis for further experiment (a colloidal explanation used as a term of reproach), and quantitative work is called for in order to test whether or not the first two effects are due solely to the value of the total osmotic pressure and to the actual concentration of potassium ion respectively. Colloidal chemistry at present abounds in such problems and " explanations " which need to be replaced by precise and quantitative conceptions and measurements, otherwise such explanations do more harm than good.

In the case of concentrated soap solutions or those to which large amounts of electrolyte have been added, the temperature coefficient of viscosity becomes extremely great, so that the viscosity at 20° may be several hundred or thousand fold greater than at the boiling point. Of course, the addition of these electrolytes tends to induce gelatinisation or, in the case of higher sodium soaps, salting out. Since salts effect the viscosity to different extents, depending upon the nature of the salt, the effect is ascribed to the anion. Obviously this requires further and quantitative elucidation.

The effect of position in the homologeous series is very marked. Even in rather dilute solution the sodium behenate ($C_{22}$) is highly viscous, whereas in the case of the laurate ($C_{12}$) only the most concentrated solution containing large amounts of electrolyte can really be termed viscous. A normal solution of potassium laurate at 20° and at 90° exhibits 8·4 and 2·8 times the viscosity of water, whereas a normal solution of potassium oleate is 1573 and 3·80 times as viscous as water at the same temperatures.

Potassium or sodium oleate ($C_{18}$) at room temperature is very much more viscous than say potassium myristate ($C_{14}$). It is probably much like the stearate ($C_{18}$) except that the effect of the double bonds is to render it liquid even at the freezing point. The effects of additions of an electrolyte is much more pronounced in the case of the oleate than the laurate, and again in concentrated soap solution as compared with dilute soap solution. In other words, it is evident that the typical effects of added electrolytes are to be attributed to their effect upon the ionic micelle and its development, concentration and composition.

Electrolytes with the common alkali ion must exert three chief effects upon a colloidal electrolyte. First the furthering of formation of ionic micelle if large quantities of simple ions are still present; secondly, driving back the dissociation with its corresponding alteration in the composition of the ionic micelle; and third, diminishing hydration of the ionic micelle.

The only mixtures which have been properly investigated are those of potassium laurate and potassium oleate. Addition of small quantities of potassium laurate to potassium oleate slightly increase the viscosity at 90°, whilst at 20°, the viscosity is greatly diminished, thus very much lowering the temperature coefficient. Such an addition must have partly the same effect of that of an electrolyte with the added complication of the possible formation of mixed ionic micelle. A mixture of equal quantities of potassium laurate and potassium oleate fairly closely resembles the pure laurate. A mixture of even relatively small amounts of laurate with the oleate causes the solution to respond to the addition of salts in a manner much more closely resembling the laurate than the original oleate.

An addition of equivalent quantities of various electrolytes the hydroxide has the greatest effect, followed by the chloride, and then the carbonate. Although if equimolar concentrations of carbonate and hydroxide are taken, the order of magnitude of the effects are the same.

It should be emphasised that other colloidal electrolytes exhibit the same typical behaviour in the addition of electrolytes as has been observed, for example, by Woudstra in the case of ferric hydroxide (chloride). According to Pauli this also is a case of a colloidal electrolyte.

An excellent example of an industrial application of this behaviour in the closely analogous case of sodium silicate is to be found in the use by Malcolmson (*Jour. Ind. and Eng. Chem.*, 1920, **12**, 174) of brine for diluting water glass whilst retaining its adhesive power. In this way a given volume of water glass could be increased by 25 per cent. without reducing its viscosity.

(b) *Density.*

Soap solutions are remarkable for their bulkiness. All soap solutions have approximately the same density as water of the temperature, and this even in extreme concentration. For example, the volume of a normal solution of sodium stearate is 31 per cent. greater than that of a solution of sodium acetate containing the same amount of water. Not only so, but we have here the almost unique case of the solution being in some cases less dense than either constituent.* For instance, a normal solution of sodium palmitate has a density equal to 0·997 of that of water of the same temperature (at 90°).

The potassium soap solutions are slightly denser than those of sodium. The ammonium soaps are somewhat lighter than the sodium soaps. The highest homologues of the fatty acids produce soap solutions of the least density. There is a steady increase as

* Compare the case of p. nitrotoluene in carbon bisulphide; Hyde, *Journ. Amer. Chem. Soc.*, *1912*, **34**, *1507*.

the homologous series is descended, with a definite break in the curve between the hexoate and the acetate, once again indicating the relatedness of the hexoate to the higher soaps. The appearance, washing power, density, and conductivity curve of potassium hexoate distinctly mark the beginning of that deviation from the behaviour of the acetate, which rapidly and regularly increases through the other members of the homologous series until it attains the typical character of the higher soaps.

It is worthy of note that the density of soap solutions does not by any means conform with the conception of electro-striction, although in these solutions there are almost as many ions and opposed electrical charges as in the case of a typical electrolyte.

(c) *Surface Tension.*

Some of the matter which might have been discussed under this heading will be referred to in paragraph 8 below, which deals with detergent action, and further, the rather extensive subject of soap films and bubbles will not be considered. Several years of further investigation would be required to answer all the questions which any chemist would at once ask with regard to the surface tension of soap solutions. The existing data are so isolated that it is still impossible to give a satisfactory broad survey of the subject. They refer, in a few instances to surface tension against air, but most of the experiments refer to surface tension at the interface with fatty or petroleum oils. In many cases the results are affected to an unknown extent by the carbon dioxide of the air, and frequently the composition of the soap is extremely ill defined, and in the experiments, for example, of Botazzi, the soap was rendered still more undefined by being submitted to a process of dialysis. Another factor which can interfere with the results is the rather ready oxidation of the unsaturated substance like the oleate. It is well worth while determining not merely the surface tension, but the actual amounts of adsorbed substance, and still further the actual composition of the " soap " in the meniscus; that is, the amounts of alkali, fatty acid, and hydrate water in the surface film. Lastly, an experimental difficulty which should be taken into account is the insolubility of the saturated fatty acids and of the acid soaps which separate out unless the solutions are kept hot.

*Soap Solution—Air Interface.*

Sodium oleate solutions in contact with the atmosphere constitute the only case in which the interfacial tension of the boundary between soap solution and a gaseous phase, has received any serious consideration. Plateau, Quinke, Marangoni, Lord Rayleigh, Milner, Hall, Harkins, Perrin, and Hillyer may be referred to in this connection, although some of the results refer to the chemical decomposition of the soap by carbon dioxide, oxidation, and hydrolysis. By far the most careful work is that of Harkins, Davies and Clark (*Jour. Am. Chem. Soc.*, 1917, **39**, 586), who, like Hillyer (*Ibid*, 913, **25**, 515), used the drop weight or drop number method. These authors found that when pure sodium oleate was added in increasing quantities to water

of surface tension 2·8 dynes per cm. at 20°, the surface tension falls at first with extreme rapidity to 24·29 dynes when 0·002 N sodium oleate has been added, but that further addition of sodium oleate causes only a slight and gradual increase of the surface tension to the value 27·20 dynes for decinormal solution. A 0·0001 N sodium oleate has a surface tension as low as 60·46 dynes and even when, to diminish hydrolysis, 0·0002 N NaOH had been added, the surface tension was still only 61·32 dynes. Similarly, a 0·008 N sodium oleate solution of surface tension 25·30 dynes still exhibits a surface tension of 31·79 dynes in presence of the comparatively large amount of sodium hydroxide 0·008 N. Harkin's conclusion is that the surface film consists largely of a single layer of sodium oleate molecules, with possibly singly and multiply charged oleate ions (ionic micelle), and hydroxyl and hydrogen ions, the film is thus entirely saturated even at low concentration of solution.

According to Hillyer the drop number of a decinormal rosin soap is the same of that of sodium oleate.

There is no recorded analysis of the composition of the substance actually adsorbed. Perrin's work in 1918 in this connection is again vitiated by the possibility that the observed effects were due to carbon dioxide.

It is worth while remembering that the power of foaming, like emulsification, is not always or entirely due to low surface tension; for instance, saponin solutions whose surface tensions are only slightly less than that of water, have a very great power of foaming on account of the formation of a solid or highly viscous film of adsorbed material in the surface.

*Soap Solution—Oil Interface.*

Here again the stalagometer or drop method has been almost invariably employed. An excellent and luminous investigation was published by Hillyer in 1903, and it was very unfortunate for this subject that his researches were not continued since his elucidations of the phenomena of surface tension and detergent action are still as convincing as ever. His papers are published in the *Journal of the American Chemical Society* which, as the writer knows from personal experience, has been inaccessible in many of the European Universities in spite of its present enormous circulation in America.

Hillyer found that in contradistinction to the behaviour of their surface tensions against air, the surface tension of sodium oleate solutions against paraffin oil (kerosene) continues to diminish rapidly and steadily with increasing concentration up to decinormal. Decinormal rosin soap like decinormal sodium oleate exhibits a surface tension which is only 5 or 6 per cent. of that of water. Decinormal sodium hydroxide has almost as great a surface tension against paraffin oil as pure water. Sodium oleate solution at 100° exhibited no marked difference in the form of curve connecting surface tension and concentration.

Hillyer also investigated the effect of excess of alkali and of acid, the former had but little effect upon any concentration of sodium oleate, whereas excess of oleic acid gradually and steadily removed

the lowering of surface tension, although even the acid oleate NaOl, HOl, causes a marked lowering of surface tension.

Finally Hillyer investigated solutions of sodium palmitate and stearate at 70° and 100°. The first traces of soap do not greatly lower the surface tension of the water but as the concentration passes through N/1000, the surface tension falls very rapidly at first and then above N/80 more gradually up to N/20 solution. This anomaly in very dilute solution was not further investigated, but was ascribed to hydrolysis. Rosin soap, whether at 100° or in the cold, does not differ markedly from sodium oleate, and is not very much affected by temperature. Both, however, exhibit a slightly developed inflexion in dilute solution like that of the stearate or palmitate.

Donnan and Potts (*Kolloid Zeitsch*, 1910, **7**, 208) measured the drop numbers of a nearly neutral paraffin oil against various concentrations of the sodium salts of the saturated fatty acids from the acetate up to the myristate ($C_{14}$). They found that the surface tension was lowered roughly in proportion to the concentration of the salts up to and including the heptoate ($C_7$). Decinormal solutions have a surface tension between 87 and 78 per cent. that of water. The octoate which appears as the lowest soap, has a much more marked effect, N/400 solution causing a lowering of 4 per cent. A N/400 myristate has a surface tension only 58 per cent. of that of water, and the curve connecting surface tension and concentration is only slightly curved. Donnan's earlier work (*Z. physikal Chem.*, 1899, **31**, 427), in which various fatty acids were dissolved in oils and their drop numbers determined against dilute alkali is explained by those results owing to the formation of soap in these experiments. This is invariably the case when commercial fatty oils come in contact wtih alkaline solutions, since they all contain more or less of free fatty acid, and it is only under these conditions that emulsification occurs.

*Soap Solution—Benzene Interface.*

Harkins, Davies, and Clark have further made exact measurements of the surface tension of sodium oleate against benzene. It falls extremely rapidly at first from the value for pure water, 35·03 dynes, through 9·00 dynes for 0·005 N, and 2·22 dynes for 0·014 N to 1·78 dynes for 0·1 N soap. It may be noticed this behaviour differs from both of those in the two interfaces already discussed. Briggs (*Jour. Phys. Chem.*, 1915, **19**, 210) has done experiments in which he measured instead the apparent amounts of sodium oleate removed from the aqueous layer, using a somewhat unsatisfactory and very incomplete method of analysis. He found a similar behaviour in that the amount removed increased only slightly in higher concentrations. Absolute results were not obtained. Briggs and Schmidt (*Ibid.*, 1915, **19**, 479) found that the optimum amount of soap for emulsification of the benzene is 1 per cent.; that is, three times the value given by Harkins, 0·01 N. Addition of 0·1 per cent. alkali favoured emulsification, but larger amounts interfered.

Shorter (*Jour. Soc. Dyer-Colourists*, **31**, 1915, 64; *ibid*, **32** (1916) 92), Shorter and Ellingworth (*Proc. Roy. Soc.*, 1916, A, **92**, 231),

showed first that potassium hydroxide has practically no effect upon the surface tension against benzene. Then he found that though the addition of oleic acid to benzene lowered the tension against water, it had no effect on the tension against soap solution, and he concluded that the surface activity of the hydrolysis alkali was only about one-fifth to one-fourth that of the undecomposed soap.

In all these cases again there is still the greatest uncertainty as to what it is that is adsorbed in the interface. In Spring's work, referred to in the section of "Detergent Action," he concluded that it was acid soap that was sorbed by lamp black, whereas filter paper sorbed alkali leaving acid soap in the solution.

Woodmansey (*Jour. Soc. Dyers Colourists*, **35**, 1901, 169) found that the amount of base sorbed from a solution of soap was greater than that of fatty acid, an acid soap remaining in the water.

(d) *The Optical Properties of Soap Solutions.*

Soap solutions constitute clear transparent solutions disturbed only by the suspended insoluble particles of acid soap resulting from hydrolysis, and exhibited in varying degrees by all soaps from caproate upwards. Here investigation (Darke and Salmon) shows that the clear liquid is not resolvable under the ultramicroscope, and that the ionic micelle is invisible in the cardioid ultramicroscope. The suspended particles of course exhibit Brownian movement, the purple ones being exceptionally active, the smallest green ones coming next. This Brownian movement serves as an excellent index to the viscosity of the liquid; it is scarcely detectable when the soap is highly viscous, and it is highly developed when most of the soap has been removed from solution as by the formation of curd. It is probable that with higher resolving power innumerable white particles would be visible, and that these constitute the particles of neutral colloid. We have detected them only when conditions of illumination, &c., were exceptionally good, just upon the limits of possible observation and they exhibited a degree of Brownian movement which corresponded to the fluidity of the medium.

Earlier investigations of the optical appearance of soap solutions whether microscopic or ultramicroscopic, have thus all had reference to the suspensions of insoluble acid soap produced in smaller or greater amounts by hydrolysis. The frequent turbidity of soap solutions has thus been an illusory proof of their colloidal nature. The insoluble acid soap may sediment out almost completely upon standing, leaving the bulk of the soap in prefectly clear transparent solution, or it may remain partly or wholly suspended in particles whose dimensions range all the way from coarse suspensions down to the smallest resolvable in the ultramicroscope. Every change of temperature or of concentration or of additions which affects hydrolysis will affect the amount of this product of hydrolysis. The acid soaps in suspension constitute an ordinary colloid.

It is now clear why Mayer, Schaeffer, and Terroine observed progressively more colloidal particles in any one soap by passing from alkaline to acid solution. Further it becomes plain why the viscosity of solutions of salts of the lower fatty acids up to the

valerianate is not markedly altered upon the addition of strong acid which liberates the soluble liquid fatty acid, although excess of base raises the viscosity. In the higher members of the homologous series, where insoluble acids and acid soaps are in question, addition of strong acids increases the viscosity appreciably through formation of colloidal acid soap; alkali does so also, although through formation of ionic micelle and neutral colloid. In accordance with this the higher soap solutions require a slight excess of alkali to clarify them completely by driving back hydrolysis. The authors named thought to identify the point of complete clarification with the point of minimum viscosity without carrying out the quantitative work and without a knowledge of the constitution of these solutions.

Lifschitz and Brandt have recently studied refractive index at 70°. They find that the refractive index varies linearly with the concentration; this held good also in the alcoholic true solutions. This undoubtedly shows that the molecular refraction is independent of whether the soap is present as crystalloid or colloid, and in the latter case is independent also of the actual constitution and of the degree of dispersion of such colloid. This conclusion was directly confirmed by the agreement of the values observed with those calculated from the atomic refractivities which, of course, have been obtained in the study of crystalloids.

(f) *Ultrafiltration and Dialysis.*

The behaviour to be expected in the ultra-filtration or dialysis of soap solutions is now clear on the basis of the theory which we have established. In the case of ultrafiltration the effect will depend largely upon which fatty acid is taken and the concentration of the soap. In dilute solution or solutions of the salts of the lower fatty acids, they will tend to pass through the filter unchanged. In more concentrated solutions of the higher soaps which contain very little crystalloid other than the alkali ions accompanying the ionic micelle, the membrane will retain practically all the soap. Intermediate cases will be particularly interesting as they will afford a direct quantitative measurement of the crystalloid matter present in such solutions.

The only published investigation is the brief note of Mayer, Schaeffer, and Terrione, already referred to, whose results were apparently in quantitative agreement with that here outlined. A systematic investigation is now in progress whose results likewise agree with prediction. Further it is readily shown that this may be made a general method for the study of hydration of colloids. It is only necessary to include in the solution to be filtered some readily analysed material which is not sorbed by the colloid and then to determine the increase in concentration of this reference substance which the filtrate exhibits. The amount of this increase affords a quantitative measurement of the total amount of water which was abstracted by the colloid from solution whether as adsorbed, or chemically combined water.

As regards dialysis, there are two points to be emphasized, the one theoretical, the other practical. In the first place the crystalloid present will be able to pass through the membrane so that in no case

will the membrane be quite impermeable to soap, and further, since dilute solutions in particular are appreciably hydrolysed, hydrolysis will be developed by the continued removal of the alkaline products of hydrolysis, leaving behind the insoluble or colloidal acid soap, the whole forming an instance of membrane hydrolysis. In the second place, however, one practical consideration vitiates the niceties of theoretical interpretation, that is that quite exceptional opportunities are afforded for decomposition of the soap by the carbonic acid from the air or from the large quantities of water employed. For instance, as we have seen Moore and Parker[16] obtained an osmotic pressure 50 times too small, and were unable to detect any alkali coming through ordinary parchment. Various other investigators, Rotondi, Botazzi, and Victoroff[27] found that acid soaps or possibly even free fatty acid remained behind on dialysis under such conditions. However, they, like Mayer, Schaeffer, and Terroine[26] found that as long as the solution was kept alkaline some of the soap did pass through the membrane.

### VI.—*Solidification and Gelatinisation of Soap Solutions.*

The solidification and gelatinisation and salting out of soap solutions afford penomena of extraordinary interest which have not received adequate interpretation in the literature.

Upon cooling, or upon the addition of various substances white opaque curd may be formed, or again, there may be obtained typical gels, clear and transparent or ranging through various degrees of cloudiness. These two very distinct forms, white curd and clear gel have always hitherto been confused with each other and referred to indiscriminately. Hence there has been controversy as to whether they were colloidal at all.

Sodium oleate solutions as studied by Miss Laing present a particularly interesting case since here it is possible to obtain one and the same solution at any one temperature in the form of transparent sol, clear jelly, or white opaque curd. The conductivity of a given soap solution is independent of whether it is studied as sol or clear gel. Again the concentration of sodium ions present is also indentical in the two cases.

We are tending towards the opinion that in a gel there exist well-developed strings of long molecules forming an exceedingly fine filamentous structure which accounts for the elasticity of gels and also for the fact that they exhibit more or less clearly oriented properties, such, for instance, as the lenticular, fairly definitely oriented, form of bubbles generated within gels. This assumed structure is, however, not resolvable under the ultramicroscope, as is only to be expected. If we are able to obtain sufficiently definite evidence for this, it would appear that the same forces are in play here as account for the phenomena of crystalline liquids and liquid crystals. There is a great deal of circumstantial evidence for this. It would serve also to explain the incipient structure which most sols develop on standing and which is such as prevents for example, definite measurements of viscosity from being taken independent

of age and rate of shear. An illustration of this general and well-known behaviour is the case of sodium behenate, where occasionally a perfectly clear and apparently homogeneous solution can be divided by pouring into two test tubes, one of which will then be found to contain practically all of the behenate, the other containing almost only water.

Freundlich in his study of certain vanadium pentoxide sols which had been aged during many years, found that at boundaries or throughout the sol, whenever the sol was set in movement, it was anisotropic and exhibited all the behaviour of a crystalline liquid, a behaviour which is likewise now attributed to the presence of long molecules, both on physical and chemical grounds. This explanation therefore links up with Bose's theory of swarms of long molecules and with Vorländers' observations that long molecules are required for the formation of liquid crystals. Sandquist's bromophenanthrene-sulphonic acid is obviously a colloidal electrolyte, analogous to soap; and solutions can be obtained under certain conditions as crystalline liquids.

These strings of molecules which we contemplate may be microns or millimetres long, in other words, they consist of innumerable molecules placed length-wise and their formation would, of course, be ascribed to residual affinity. The very strong tendency of soaps to form such structures is proven by the manner in which they form filamentous and fibrous curds (*see below*). We investigated several sulphonates containing up to 10 carbon atoms, but as these are ring compounds, the development of ionic micelle was only very slight, and the solutions crystallised without tendency to form fibres.

The ultramicroscopic investigation of soap gels presents some difficulty, since it is difficult to know when it is a real gel that is being observed. Probably all of Zsigmondy and Bachmann's[29] work (like our own) refers to curds. A gel is probably optically clear apart from the particles which result from hydrolysis and which are, of course, devoid of motion on account of the high viscosity of the soap solution. Nevertheless in one undoubted instance, we observed and photographed a cloudy gel of sodium oleate which, in addition to curd fibres, contained an exceedingly fine and delicate filamentous network. The quartz surfaces in contact with these sodium oleate gels often exhibit indefinitely long and exceedingly fine filaments just on the limits of visibility and just capable of being photographed with long exposures. Their regularity of form and texture is astounding. They simulate living matter in their appearance; they may take the form of a simple sine wave, or of regular waves with higher harmonic series superimposed on them. Any one part of such a filament is identical in form and structure with any other part. They are probably derived from originally straight just resolvable translucent tubes containing very regularly spaced whitish dots or lengths.

The beautiful pioneer observations of Zsigmondy and Bachmann on soap curds and our own studies, in which the cinematograph was combined with the ultramicroscope in order to follow the genesis

and life histroy of the various structural elements, have shown that soap curds consist invariably of fine fibres.

In the case of all sodium soaps these may be many centimetres in length, and may be straight or characteristically curled but they are never of greater thickness than about 1 micron. Most of them are of ultramicroscopic diameter, and the thicker ones may be always or usually merely parallel bundles of finer ones These fibres are often so fine that shorter or unattached fibres exhibit Brownian movement when the medium is not too viscous. These curd fibres constitute the only mechanical structural element of sodium soap curds and represent the stable condition of such curds even after the lapse of years.

The potassium soaps are somewhat more complicated and the phenomena require more time for development. Upon slow cooling, minute V-shaped twin fibres appear of about a few tenths of a micron in diameter, but never more than a few hundredths of a millimetre in length as compared with the inch-long fibres of sodium soaps. These twin fibres however, do not constitute the stable solid phase in potassium soap solutions for, on standing for a few days, they gradually become replaced by thin irregular leaflets or crystals less than 1 micron in thickness.

The curd fibres of sodium soaps may scarcely be called crystals, nevertheless they constitute a sufficiently definite phase to exhibit some of the properties of crystals. For instance, they appear to exhibit a definite solubility at each temperature. A curd of sodium soap therefore in general consists of a felt of curd fibres in which is enmeshed an aqueous liquid containing, according to the temperature, traces of soap and alkali, the product of hydrolysis, or perhaps large amounts of soap sol or gel depending upon age, previous history and, of course, temperature.

At the temperature of initial solidification only a few fibres are formed, the bulk of the soap remains in the solution which therefore exhibits a practically undiminished vapour pressure and conductivity. As the temperature is lowered, the solubility of the curd fibres rapidly diminishes until the enmeshed liquid consists chiefly of water and its vapour pressure and conductivity behave accordingly. Throughout this range of temperature the stable condition of the soap solution is the formation of the appropriate amount of curd fibres with enmeshed gel. The definite solubility of the curd fibres at any one temperature is evinced by the fact that the conductivity of a well-aged curd is approximately independent of the concentration of the original soap.

It follows from the above conception based upon direct measurements that different concentrations of any one soap cannot solidify at the same temperature, but this depends upon the temperature-conductivity curve of the curd fibres. The lower the concentration of the soap, the lower the temperature of initial solidification.

It is a remarkable fact to which Krafft and Wigelow[17] called attention, that there is a certain parallelism between the initial solidification temperature of a sodium soap solution and the melting point of the pure anhydrous fatty acid from which the soap is derived.

This is strictly true for only one concentration. Rather concentrated soap solutions have an initial solidification temperature which is very near the melting point of the fatty acid, dilute solutions of course fall much below it, whilst, as we have found, highly concentrated soap solutions come distinctly above it. No tenable explanation of this behaviour has been put forward. It is probable that the soap fibres consist of hydrated neutral colloid and that the slight alkalinity of the mother liquor is due to the particles of acid soaps resulting from hydrolysis and which we have so often referred to. There are particles in fact still visible under the ultramicroscope leading an independent existence in the wet curd, and it is amusing to watch a small particle performing violent Brownian movement up and down the length of a curd fibre from whose neighbourhood it often has difficulty in escaping. This form of Brownian movement has not previously been described. The coincidence with regard to melting points refers of course, only to sodium soaps.

It is worth while emphasizing that neither gelatinisation nor formation of curd is identical in kind with the process of attainment of equilibrium within the liquid sol. A true reversible equilibrium is attained from both sides within the sol whilst it is supersaturated with respect both to gelatinisation and formation of curd.

Several authors have observed that formation of curd is accompanied by the evolution of heat.

## VII.—*The Effects of Additions.*

### (a) *Excess of Fatty Acid.*

In the case at least of the saturated fatty acids, the addition of excess of acid results in the formation of acid sodium or potassium salts which are insoluble. These acid soaps probably do not correspond to any very definite chemical formula and as yet no complete chemical analysis of such a specimen has been obtained from which, for example, the amount of water in it could be deduced. As regards amount of alkali, their composition lies between that of the acid salt exemplified by the acid sodium acetate, $NaHAc_2$, and that of neutral soap. These acid soaps do not lie within the region investigated from the standpoint of the phase rule by Donnan and White,[19] who showed incidentally that possibly no pure acid sodium palmitate $NaHP_2$ exists.

In the case of sodium palmitate, we have found that addition of palmitic acid to the solution causes a change in the conductivity and also in the vapour pressure. Both conductivity and lowering of vapour pressure when plotted against the amount of acid added, are seen to diminish linearly to a small value at a point corresponding roughly to HP·2NaP. At this point the magnitude of the conductivity and lowering of vapour pressure although small is definite and independent of the original concentration of the sodium palmitate. This behaviour clearly points to the formation of the insoluble acid soap HP·2NaP, in equilibrium with its saturated solution. Further addition of palmitic acid causes both the lowering of vapour pressure and conductivity of the aqueous fluid to become still smaller, showing

that the acid soap becomes more and more insoluble as the amount of acid in it increases beyond the composition mentioned. These " solutions " appear as translucent pastes or jellies at 90°. On cooling silky fibrous crystals of acid soaps may separate. More dilute solutions froth very readily.

(b) *Excess of Sodium Hydroxide.*

Most of the phenomena occurring upon the addition of caustic soda or other electrolytes, which ultimately result in the quantitative salting out of the soap from the solution, will be discussed in Part II., which deals with the technical colloidal chemistry of soaps, their solutions, gels, and curds.

Rarely are homogenous solutions of soap to be met with during the process of manufacture, since these would be of prohibitively great viscosity. Usually, as has been found in this laboratory, the soap is in the form of an emulsion of two soap solutions, whether sol-sol, sol-gel, or sol-curded gel. The experimental evidence will be published elsewhere.

A number of theoretical points also must be reserved for forthcoming publications. However, it should be mentioned here that for the greater part these additions do not actually combine with the soap, but drive back its dissociation or displace the numerous equilibria involved.

## VIII.—*Detergent Action of Soaps.*

The brilliant work of a number of such investigators as Hillyer (1903) and Spring (1908) has shown conclusively that the detergent power of soaps is due to their colloidal nature, and it is only influenced by their chemical constitution in so far as this affects their behaviour as colloids.

In commerce soaps are usually bought and sold upon their appearance and texture after assurances have been given with regard to their classification as curd soaps, tallow rosin soaps, cleanser soaps, &c. There are no universally accepted quantitative standards to which soaps are referred with regard to their washing power. It is convenient to give a list of all the cognate experimental methods hitherto published as having more or less bearing upon this question :—

(1) Measurement of surface tension against air by capillary tubes or by drop members or by bubbling or by measuring the amount of froth produced under definite conditions.
(2) The measurement of surface tension against oil or paraffin oil or benzene by drop numbers or measurement of emulsification.
(3) Measurement against carbon or other powders by measuring rate of sedimentation or protective action in filtration.
(4) Protective action as measured by gold numbers.
(5) Direct washing experiments with specially soiled clothes under controlled conditions of true temperature and concentration. (*Zhukov and Shestakov. Chem. Ztg.*, 1911, **35**, 1027.)

It is, of course, impossible to give here a summary of the mass of information, chiefly of a technical character, with regard to the detergent action of various soaps and soap substitutes and their effect upon various textiles, but the chief theoretical results will be referred to.

Krafft has quite rightly insisted that the soaps must be in solution in order that such solutions should exhibit appreciable detergent action. Thus in cold water sodium palmitate and stearate are nearly insoluble, whilst the soluble oleate is an ideal detergent, and even the only moderately soluble laurate and rosinate wash fairly well. Hot water is necessary for the use of tallow soaps, which consist largely of palmitate and stearate; as Jackson (Cantor Lecturer) has pointed out, potassium soaps are more soluble in the cold than sodium soaps. We would add here the deduction from our measurements of the amount of ionic micelle present in various pure soap solutions, that the washing power which the oleates exhibit *par excellence* is connected with the fact that their colloidal nature persists well into dilute solutions; whilst the laurate in dilute solutions and more especially at higher temperatures is largely broken down to simple electrolyte. For this reason, stearate is suitable for washing at the boiling point, since at this temperature it is soluble and it contains much more colloid than the lower soaps. Such considerations are of importance, for example in the choice of a suitable soap for the washing of woollen goods in the cold.

Earlier theoretical writers, such as Chevreul, Berzelius, Persoz, von Bussy, Waren-Delarne, Knapp, Stiepel and Moride emphasized the emulsifying powers of soap solutions and of soap foam towards fats and fatty materials. The capacity of soap solutions to wet oily matter was also emphasized whilst the unknown amount of hydrolysis alkali was credited with powers of saponification.

Hirsch, in 1898, showed experimentally that fatty oils were not more readily emulsified than were various other organic liquids, and he demonstrated also that the large amount of oil emulsified was quite out of proportion to the small amount of soap present. This showed that the effects produced were ascribable to the soap itself and not to any alkali present.

Donnnan (*Zeitsch physical Chem.*, 1899, **31**, 42) showed experimentally that emulsification and lowering of surface tension went hand in hand in the case of solutions of different soaps. Plateau had pointed out that in general formation of solid surface films might be quite as effective as low surface tension in emulsification.

Hillyer (*Jour. Amer. Chem. Soc.*, 1903, **25**, 511, 524, and 1256) showed experimentally that the emulsifying properties of soap could not be attributed to hydrolysis alkali hydroxyl ions, nor did alkali possess the power of wetting oily matter that soap did. Hence both these factors in detergent action must be due to the soap itself. Of course, as Donnan had pointed out, the free fatty acid contained in all natural fats and fatty oils could be neutralised with formation of soap this would be quite different from saponification of glycerides which is an extremely slow reaction. Hillyer demonstrated again the parallelism

of low-surface tension and emulsification in the case of soaps, and incidentally showed that saponin emulsified through formation of solid surface film instead of through low surface tension. Hillyer also demonstrated the power of penetration into capillary interstices which is conferred upon soap solutions by their very low surface tension.

We have then experimental proof of the operation of two of the previously assumed factors of detergent action, emulsification (parallel to low surface tension), and wetting power, both ascribable to the undecomposed soap itself. The third suggested factor, the action of soap in making tissue and impurities less adhesive to one another was also put forward again by Hillyer, but the experimental evidence is entirely due to Spring (*Kolloid, Zeitsch*, 1909, **4**, 161; 1909, **6**, 11, 109, 164; *Arch. Sci. phys. nat.*, **28**, 569; **29**, 41, **36**, 80; *Rec. trav. chem.*, **29**, 1; *Bull. acad. Roy. Belg.*, 1909, 187, 949; 1911, **24**, 17). Goldschmidt has already postulated a protective action of the colloidal soap upon dirt particles, since Zsigmondy had shown that the gold number of sodium stearate (the minimum quantity to protect 10 c.c. of red gold sol from colour change upon addition of 1 c.c. of 10 per cent. sodium chloride solution) was 10 mg. at 60° and 0·01 mg. at 100°. The value for sodium oleate was 0·6 to 1 mg.

Spring pointed out that all previous workers had been imbued with the conception of dirt as being of a fatty or oily nature, or covered with a coating of such nature. In his experiments, therefore, he carefully eliminated all fatty matter, which leaves the detergent action of soap quite unimpaired. His striking and original experiments dealt with purified lamp black, silica, alumina, and iron oxide.

Spring's conception is that carbon promotes the hydrolysis of a soap solution and forms a stable non-adhesive sorption compound with the acid soap produced. Dirt upon a fabric he regards as being combined with the fabric in an analogous way. Cleansing by soap is simply the formation of a sorption compound dirt and soap in place of the sorption compound dirt and fabric by direct substitution. A more logical alternative is that of double decomposition in which two sorption compounds are formed, fabric + soap and dirt + soap. As a matter of fact it is often extremely difficult to remove soap from a fabric after the operation of washing. Spring points out that alcoholic solutions possess poor detergent power because hydrolysis is not so great, this is not true if the alcoholic soap is used in water. However, he found that whilst lamp black took up acid soap, ferric oxide, silicic acid, and cellulose take up soap containing an excess of alkali, so that his results in some cases might be more logically attributed to soap itself. The basic soaps of which he speaks do not in fact exist. The poor detergent action of alcoholic soaps on this view would simply be ascribable to the fact that in alcohol the soap contains only traces of colloid.

Spring's two chief experimental results, are that lamp black is carried through filter paper which, in the absence of soap, would retain it completely, and, secondly, that the rate of sedimentation is a function of the concentration of soap or, indeed, of alkali present. Lamp black sedimented as fast in 2 per cent. soap solution as in water, whereas in 1 per cent. solution it remains suspended for

months, and in $\frac{1}{2}$ per cent. solution for days. In the case of ferric oxide, the optimum concentration was $\frac{1}{2}$ per cent. soap, and in the case of potters' clay, 1/32 per cent. soap. Alumina showed remarkable periodic optima in 1/4, 1/8, and 1/16 per cent. soap, with a similar numerical periodicity of coagulation. Zhuknov and Shestakov found that in laundry practice the best results were obtained with 0·2 to 0·4 per cent. soap solution.

Donnan and Potts found a similar optimum concentration in the emulsification of paraffin oil by soap solutions in a concentration of N/300. They emphasize that the excess of soap in the interface which is a necessary corollary of the lowered surface tension and the viscous nature of the surface film must both contribute to the stability of the emulsions. Pickering (*Jour. Chem. Soc.*, III., 86) agrees both with Donnan and Spring, but considers also that oil and other substances are soluble in the presence of soap.

Jackson (*Jour. Soc. Arts*, **55**, 1101 and 1122 (1908), Cantor Lectures) called attention to the influence which soap exerts upon the state of subdivision of the dirt, and he observed under the microscope dirt particles and fibres of linen being brought first into oscillation and then completely loosened by a soap. This spontaneous action was best exhibited by an alkaline oleate. He also, pointed out that the presence of glycerine in soaps had only an unimportant influence upon their detergent action.

Shorter (*loc. cit*) adduces experiments from which he concluded that acid soaps exhibit no surface activity and that detergent action is due mainly to undecomposed soap. Excess of alkali enhances the detergent action. Developing the consideration of the electrical effects introduced by Donnan and Potts (*loc. cit*), he points out that the effect of the alkali is to increase the negative charge both on the particles of oil and dirt and on the surface to be cleansed, which tends to prevent coagulation and redeposition of those particles.

It emerges from all this discussion that there are a number of definite factors in detergent action; first, the necessity of having the soap in solution; second, power of emulsification which goes parallel with low surface tension and the formation of surface films; third, wetting power which like the last, is ascribable to the undecomposed soap itself; fourth, the action of soap in forming non-adhesive colloidal sorption compounds with tissue and impurities due sometimes to acid soap, but more often to soap itself and capable of remaining in stable suspension; fifth and lastly, it is an essential in all cases that the soap should be in colloidal form.

It is evident that comprehensive quantitative work is necessary to complete and co-ordinate the existing fragmentary work in any one case. Each of these factors are perfectly capable of simultaneous determination and quantitative evaluation.

## IX.—*Retrospect.*

We have seen that all the phenomena of soap solutions point to the existence of a highly conducting heavily hydrated ionic micelle of the general formula $(NaP)_x \cdot (P')_n \cdot (H_2O)_m$; and that from

the scattered indications in the literature it is evident that many colloidal substances of great industrial importance must exhibit similar behaviour and be classed together with soaps as colloidal electrolytes.

This conception leads then to the following complete circle of continuous transitions between types of solutions and sols through each of the well-recognised intermediate types. For convenience, the circle is given as a table. The + signs indicate the relative extent to which osmotic pressure and conductivity are exhibited by the various standard types. The table is intended to represent the natural sequence of transition in which consecutive pairs are much closer than non-consecutive pairs. Thus there is evidently a gradual transition from neutral colloid through semi-colloid (not through charged colloid or colloidal electrolyte) to ordinary crystalloid, that is, non-electrolyte. Some of these transitions may be realised in the case of soap solutions by merely altering the concentration or temperature or by passing from one member of the homologous series to another.

TABLE I.

*Circle of Continuous Transition between Types of Solutions and Sols.*

| Group. | Examples. | Osmotic Activity. | Conductivity. |
|---|---|---|---|
| Crystalloid, non-electrolyte | Sucrose | + + + | 0 |
| Semi colloid | Dextrines | + | 0 |
| Neutral colloid | Pauli's egg albumin | 0 | 0 |
| Charged colloid | Gold sol | + | + |
| Colloidal electrolyte | Soap, dyestuffs | + + | + + + |
| Crystalloidal electrolyte | KCl | + + + | + + + |
| Electrolyte | $HgCl_2$ | + + + | + |
| Crystalloidal non-electrolyte. | Sucrose | + + + | 0 |

The conception here presented of the constitution of soaps and their solutions, gels, curds, and sediments is only a preliminary sketch but its main outlines would appear to be authenticated by experiment.

SELECTED REFERENCES.

Free use has been made in the text of the various investigations carried out in this laboratory, a number of which have not yet appeared, and a few of which are not yet completed.

I.—*Conductivity.*

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Conductivity of dilute solutions of sodium oleate, potassium stearate and potassium palmitate. Freezing points of N/8 and N/16 sodium oleate. Boiling point experiments showing that the method was unreliable.

2. J. W. McBain and M. Taylor. (Zeitschr. physikal Chem. 1911, **76**, 179)

Very painstaking measurements of the conductivity of sodium palmitate in all concentrations, sodium, acetate, sodium hydroxide, sodium palmitate with excess of hydroxide and of palmitate acid; boiling point determinations showing that the method was inapplicable, to a vapour pressure measurement in which the vitiating influence of dissolved air was largely eliminated; salting out experiments and analyses of sediments.

3. J. W. McBain, E. C. V. Cornish, and R. C. Bowden. ('Trans. Chem. Soc.' 1912, **101**, 2042.)

Conductivity and densities, solidification, temperatures and appearance of sodium laurate and myristate at various temperatures.

4. R. C. Bowden. ('Trans. Chem. Soc.' 1911, **99**, 191.)

Conductivity of sodium stearate at 90°.

5. A. Reychler. ('Kolloid Zeitschr.' 1913, **12**, 277; 16th 'Vlaamsch Nat' Gen. Congres, Leuven,' 1912, 69; '8th Intern. Congress App. Chem.' 1912, **22**, 221; 'Bull. Soc. chim. Belg.' 1913, **37**, 300; **27**, 217; **26**, 193, 485; **27**, 110, 113.)

Conductivity of sodium palmitate, cetyl sulphonic acid, sodium cetyl sulphonate, cetyl sulphonate of tri-ethyl cetyl ammonium, hydrochloride of di-ethyl cetyl amine, tri-ethyl cetyl ammonium iodide, sodium oleate. Boiling points of the frothing solutions of many of the above, unreliable. Sediments in sodium palmitate solutions, extractability of sodium oleate solutions by toluene.

6. F. Goldschmidt and L. Weissmann. ('Kolloid Zeitschr,' 1913, **12**, 18; 'Seifensieder Zeitung,' 1914, **41**, 337.)

Conductivity and viscosity of the ammonium soaps of the fatty acids of palm kernel oil at various temperatures and concentrations, with and without additions of ammonia and ammonium chloride.

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Conductivity and viscosity of the potassium soaps of the fatty acids of palm kernel oil with and without additions of potassium hydroxide and potassium chloride.

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Conductivity, density and appearance of potassium salts of the fatty from the acetate to the stearate at 90°.

9. J. Kurzmann. ('Kolloidchem. Beiheft.,' 1914, **5**, 427; Dissert. Karlsruhe. 1914.)

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10. K. Arndt and P. Schiff. (Kolloidchem. Beihefte. 1914, **6**, 201.)

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11. H. Pick. (Seifenfabr. 1915, **35**, 255–7, 279–81, 301–5, 323–5.)

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Conductivity and boiling point measurements of dry alcoholic solutions of potassium oleate and of oleic acid.

13. McBain, M. E. Laing and Titley. (' Trans. Chem. Soc.' 1919, **115**, 1279.)

Conductivity, density, and freezing points of potassium, laurate, oleate, octoate, acetate and decoate and of sodium oleate and acetate. Formulation, concentration and mobility of the ionic micelle. Dew point measurements of ammonium laurate and palmitate and of potassium chloride, laurate, octoate, and oleate at 20°.

14. J. W. McBain and C. S. Salmon. (' Proc. Roy. Soc.' and ' Journ. Amer. Chem. Soc.,' March 1920.)

Dew point measurements of most of the sodium and potassium soaps down to the acetate at 90°. Formulation, concentration and mobility of the ionic micelle.

15. J. W. McBain, M. E. Laing and M. Taylor. (Not yet appeared.)

Conductivity, dew point and density of sodium palmitate solutions containing various additions of sodium hydroxide and of palmitic acid.

## II.—*Molecular weight and Osmotic activity.*

1, 2, 5, 12, 13, 14, 15 above.

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Osmometer experiments with soaps giving unreliable and erroneous results, in some cases of the wrong order of magnitude.

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Ebullioscopic measurements of the sodium and potassium salts of most of the fatty acids in water and in alcohol, in most cases vitiated by the partial pressure of air in the soap bubbles. Salting out. Extractability with toluene. Appearance and sediments Effect of carbon dioxide.

18. A. Smits. (' Zeitschr. physikal. Chem.', 1902, **39**, 385; 1903, **45**, 608.)

Tensimetric determinations of sodium palmitate vitiated by partial pressure of air present.

19. W. M. Bayliss. (' Proc. Roy. Soc.', 1910, B, **81**, 269.)

F. G. Donnan and A. B. Harris. (' Trans. Chem. Soc.', 1912, **99**, 1,554.)

Conductivity and osmometer measurements with Congo-red.

## III.—*Hydrolysis.*

20. J. Lewkowitsch. (' Zeitschr. Angew Chem.', 1907, **20**, 951.)

The hydrolysis of soap solutions could never be complete since it was impossible to extract all the fatty acid by shaking with another solvent.

21. D. Holde. (' Zeitschr. Elektrochem.', 1910, **16**, 436.)

Extraction of aqueous alcoholic soap solutions by petroleum ether *See* 2 above.

22. G. Fendler and O. Kuhn. (' Zeitsher. angew. Chem.', 1907, **22**, 107.)

Effect of carbon dioxide upon various soaps. *See* 17 above.

23. F. Goldschmidt. (' Chemiker. Zeitung.', 1904, 302.)

Hydrolysis in aqueous alcoholic solutions of soap

24. J. W. McBain and H. E. Martin. (' Trans. Chem. Soc.', 1914, **105**, 957.)

Determinations of hydrolysis alkali by hydrogen electrode in sodium hydroxide, sodium and potassium palmitates, potassium myristate to acetate, with and without excess of palmitic acid or alkali or sodium chloride at various temperatures and concentrations and some commercial soaps at 90°.

25. J. W. McBain and T. R. Bolam. (' Trans. Chem. Soc.', 1918, **113**, 825.)

Determination of hydrolysis-alkali by rate of catalysis of nitrosotriacetonamine in sodium acetate and palmitate with and without added sodium hydroxide and of potassium palmitate at various temperatures and concentrations.

IV.—*Viscosity.*

6, 7, 9, 10, above.

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Surface tension, viscosity and appearance of a dialysed Marseilles soap of unknown composition, with and without addition of alkali.

28. F. D. Farrow. (' Trans. Chem. Soc.', 1912, **101**, 347.)

Viscosity of sodium palmitate solutions at 70° in various concentrations with and without additions of palmitic acid, sodium hydroxide, sodium chloride or potassium chloride.

V.—*Optical.*

29. R. Zsigmondy and W. Bachmann. (' Kolloid. Zeitschr., 1913, **11**, 145.)

Ultramicroscopic observations of the formation of curd in aqueous and alcoholic solutions of sodium and potassium oleate, stearate and palmitate, also solubilities and sediments and solidification temperatures.

30. J. Lifschitz and J. Brandt. (' Kolloid-Zeitsch.', 1918, **22**, 133.)

Refractive index of sodium stearate, palmitate and oleate solutions and of potassium palmitate in various concentrations at 70°.

[Note.—The subject of soap manufacture will be dealt with by Prof. J. W. McBain and Mr. Ernest Walls in the 4th Report of the Committee.—W. C. McC.L.]

## ULTRA-MICROSCOPY: DEGREE OF DISPERSION—MEASUREMENT WITH THE ULTRA MICROSCOPE.

*By* George King, M.Sc., F.I.C.

The physical and chemical phenomena observed in colloidal solutions, depend upon four factors: the *concentration* of the disperse phase, its *size*, *shape*, and *internal structure*. A knowledge of these factors is desirable in order that the phenomena observed in any particular investigation may be interpreted in terms of the energy distribution in the system.

(a) *Concentration of Disperse Phase.*

The concentration is often determined by the evaporation of the dispersion medium—this method is satisfactory only in the absence

of non-volatile substances of molecular dimensions. The concentration of the disperse phase in hydrosols is most conveniently determined by ultra-filtration through collodion membranes. The method used by Zsigmondy[57] gives very accurate results and is less complicated than the Bechold[2] method. By suitably varying the composition of the collodion (Schoep[35]), a rough grading of a non-uniform disperse phase is rendered possible, those colloidal particles above a definite size only, remaining on the filter. Certain physico-chemical methods, such as colorimetric determinations have been successfully used to determine concentration and Marc[34] has developed the interferometer for technical use, whilst Mecklenburg[25], and more recently, Tolman[48], have used the intensity of the light scattered by a colloidal solution (Tyndall Beam[31]).

(b) *Size, Shape, and Internal Structure.*

The size of the particle more than any other property determines the behaviour of a particular solution, and its estimation is therefore of considerable importance.

According to Ostwald the dimension is best expressed as the degree of dispersion, or, the ratio of the absolute surface of an individual particle of the disperse phase, to the volume of that particle. von Weimarn[50], however, has pointed out that this ratio alone does not sufficiently determine the properties of the system, on account of the difference in the internal structure of two otherwise similar particles. Moreover the shape and hence the value of the ratio, depends upon the method used for the preparation of the colloid (Svedberg, Gans[12]). Since nothing definite is known of the internal structure and shape of the particle under particular experimental conditions, it is more usual to express the size in terms of the linear dimensions of the particle. The method used for this determination depends upon (1) the physical condition of the continuous phase and the size of the particle, (a) microscopic, (*b*) sub-microscopic. Suspensions containing particles as large as 10 $\mu = \cdot 01$ mm. exhibit colloidal properties—*e.g.*, Brownian movement, cataphoresis—and for the purpose of classification, such particles are called *microns*[58]. The lower limit for the micron is conventionally fixed at $\cdot 2\ \mu$ and corresponds with the limit of microscopic visibility as determined by Johnston Stoney[19]. *Sub-microns* are detected by means of the ultra-microscope, and range from $\cdot 2\,\mu$ to the lower limit $3\,\mu\mu = \cdot 000003$ mm. observed by King[20] using the Zsigmondy[59] immersion ultra-microscope.

I.—*Continuous Phase Solid.*

(a) *Microns.*

Owing to the absence of Brownian movement, direct microscopic measurements can be made. Tinker[47] using an oil immersion fluorite objective, and improved illumination, was able to measure the particles in a semi-permeable membrane up to the theoretical limit of microscopic visibility.

(b) *Sub-Microns.*

Two methods each depending upon the application of the Tyndall effect are available, but they cannot be applied to the non-transparent solid solutions encountered in metallurgical practice.

1. *Rayleigh's Formula.*—It is well known that an incident beam of light falling upon particles, small compared with the wave length of light, is not reflected but scattered and polarized. The intensity of the scattered light varies according to the Rayleigh[32] formula $I_s = Anr^6/\lambda^4$ where A is a factor which depends upon the experimental conditions, " n " is the number of particles of radius " r " scattering light of wave length " $\lambda$ " With a particular solution where "n " is constant and the intensity of the scattered light may be measured by means of a spectrograph and " r " found by substitution in the Rayleigh formula. The method is considered by Henri[15] to be very sensitive and to give exact results with hydrosols. But it is neither so convenient nor so rapid as the method elaborated by Zsigmondy[59] in his investigation of gold ruby glass and for which, in collaboration with Siedentopf[36] the first ultra-microscope was designed.

2. *Ultra-Microscopy.*—Zsigmondy observed the scattered light in a microscope set orthogonally to the illuminating beam. The particle then looks like a planet, self-luminous in a dark field. The light observed is sometimes coloured[60] and appears as diffraction rings, the size and colour of which is independent of the size of the particle, but depends upon the numerical aperture of the objective and condenser, and the intensity of the illuminating beam. The light used must be of high specific intensity, and the illumination system such that in the solid under examination, a layer of known thickness, and less than the depth of vision in the microscope, is illuminated, by a beam of known width. Suitable apparatus made by Zeiss[56] and Reichert[33] is known as the Zsigmondy " slit " ultra-microscope, and the method of manipulation has been well described by Heimstädt.[14]

The solid solution to be examined is cut so as to form at parallelopiped some 3 mm. thick, with two carefully polished faces at right angles. This is placed on a special microscope stage so that the illuminated layer can be observed at any point in the parallelopiped. By direct counting it is then possible to determine the number of particles " N " in unit volume of the solid, containing a mass " M " of the disperse phase of density D. By substitution in the formula $L = \sqrt[3]{\frac{M}{DN}}$ the linear dimension of the particle, considered as a cube,i s calculated (*c.f.* Wiegner[54]). Errors may be introduced in the determination of density and mass. It is usual to assume that the density is constant and independent of the size of the particle, and accordingly the ordinary density of the substance in microscopic condition is used. For metal sols in solid solution the error, if any, is negligible (Cholodny[7]), but for oxides, hydroxides, and emulsions this assumption may introduce an error making he estimated size too large (Wintgen[55], Büchner[4]). The determination of mass per

unit volume in solid solutions gives the total mass of submicrons and also amicrons* present. Since the amicrons are not included in the number of particles counted, their mass should be subtrated in order to obtain the true concentration of the submicrons. For solid solutions there is no satisfactory method of correcting for this error, but with hydrosols it is possible to separate the amicrons by ultra-filtration, and it is found that the error they introduce does not affect the order of the magnitude, and is seldom more than 50 per cent. The more recent ultra-microscopes cannot be used for the examination of solid substances.

II.—*Continuous Phase Liquid.*

(a) *Microns.*

1. *Filtration.*—For the rapid grading of microns filtration through special earthenware filters is convenient, this was the method of Linder and Picton[22] (1892). Bechold[2] extended the method by preparing a series of graduated filter papers which are standardised for known solutions, and used under pressure in a special apparatus.

2. *Stokes' Law.*—The viscous resistance of spheres of radius " r " density " $\rho$ " moving with uniform velocity " v " in a medium of density $\rho^1$ and viscosity $\eta$ is given by Stokes' Law $F = 6\pi\eta rv$. This Law was first applied to colloidal solutions by Barus and Schneider (1891) to measure the radius of particles precipitated by electrolytes. Since the force acting is gravity " g " the equation becomes—

$$r = \sqrt{\frac{g}{2}\frac{\eta v}{\rho - \rho^1}},$$

It was shown by Perrin[30] that Brownian Movement does not interfere with the mean velocity of the particle in colloidal suspensions and solutions so that, assuming they are spheres, we have a ready means of determining accurately their size from diameters of 1 mm. to and beyond the microscopic limit.

(b) *Sub-Microns.*

Methods may be classified as (1) ultra-filtration; (2) ultra-microscopy; application of single reflecting condensers, using (3) Stokes' Law; and (4) density of distribution; (5) double reflecting condensers for direct measurement; (6) improved ultra-microscopy; application of (7) light absorption; (8) Rayleigh Formula; (9) diffusion constant.

1. *Ultra-Filtration.*—Bechold's method (referred to under Microns) may be used but the prepared papers, owing to the negative charge in the capillaries, cause adsorption and precipitation of the positive colloid.

2. *Ultra - Microscopy.* — The Zsigmondy - Siedentopf apparatus (described above) was adapted for the examination of liquids and gases by introducing an observation cell. This cell—improved by

* The term amicron is used for particles which cannot be detected in the ultra-microscope.

Thomac[46]—is provided with quartz windows at right angles and held in a special clip so that the condenser and water immersion objective are directly opposite the windows. On account of the Brownian Movement it is more difficult with liquids than with solids to count the particles in a known illuminated volume. The solution should be so diluted, that at the same time, about four particles only are visible and ten momentary counts are made. The solution in the cell is changed ten times, counted each time, and the mean of the 100 counts is found. A control observation should be made with a different dilution. With experience the total time required for a determination is about 30 minutes, and it is recommended by King[20], that for rapid work, momentary illumination by means of a pendulum be used, and the momentary observations recorded on a typewriter. With this apparatus hydrosol submicrons of $2\mu$ to $5\mu\mu$ can be measured, provided the refractive index* of the particle is sufficiently different from that of the water—a proviso which applies to all ultra-microscopic observations.

Shortly after the introduction of the "slit" ultra-microscope other systems of dark ground illumination, well known to earlier English microscopists, were used for the examination of colloidal solutions. These systems differ from the Zsigmondy arrangement in that the illuminating beam is coaxial with the microscope, and is brought to a focus in the colloidal solution by means of a special substage condenser, provided with a central stop, so that the solution is illuminated from all sides by rays comprised within the apertural zone of 1·0 to 1·3 NA. It is evident that the value of the apertural zone need not be greater than the refractive index of the medium, *e.g.*, for hydrosols 1·33. The earlier condensers of this type are of historical interest only, as also are the Cotton and Mouton[8], Scarpa[34], and modified Abbe condensers used with centre stop objectives of high numerical aperture. Reference should be made to the useful summary by Burton[5].

The substage ultra-condensers suitable for colloidal solutions or the observation of living and unstained bacteria may be classified as (1) single reflecting, Reichert and the Zeiss Paraboloid[37]; (2) double reflecting, Leitz[23]-Jentzsch[18]; and Zeiss Cardioid[38].

1. *Single Reflecting Condensers.*—The Reichert and so-called paraboloid† although different in principle have both the same uses and limitations. They are suitable only for comparatively coarse hydrosols, and cannot be used for direct quantitative estimations, since both show spherical aberration and in the paraboloid the images produced by the different zones vary in size. Consequently the intensity of illumination decreases from the centre of the field. Owing

* The intensity of scattered light

$$I_s \propto \left[\frac{\mu_1^2}{\mu^2} - 1\right]^2$$

where $\mu$ is the refractive index of medium, and $\mu_1$ of the submicron.

† Siedentopf modified the shape of the true Paraboloid of Wenham (1584) and so made the technical reproduction of the condenser cheaper and less tedious.

to the fact that both of these condensers do not focus at a sharp point, but rather build up a patch or fleck of light, no difficulty is experienced in the centering of the condenser, and although the thickness of the microscope slide or observation chamber may be varied slightly (0·3 mm.) this does not seriously interfere with the observation. The illumination used is either an inverted incandescent gas mantle or a Nernst lamp. For the rapid examination of a series of solutions the paraboloid is not so convenient as the Zsigmondy arrangement since the microscope setting must be distrubed after each reading and the slide and cover glass most carefully cleaned. For use with the Reichert instrument a small observation cell has been constructed through which a series of solutions may be passed.

3. *Stokes' Law.*—Although useless for direct quantitative work, Reichert and Paraboloid ultra-microscope when arranged horizontally, are well suited for the purpose of determining the radius of sub-microns from their speed of settlement by the application of Stokes' Law (*see above under* Microns). The method cannot conveniently be used for submicrons of less than $20\mu\mu$ diameter since calculation shows that gold particles of this size take seven hours to fall 0·1 mm. By super-imposing on gravity an electrical field, the speed of settlement is increased and Burton[6] by this means has applied the Law to the " weighing of the particles " (*c.f. also* Westgren[53]).

4. *Density of Distribution.*—These instruments may also be used to count the number of particles n and n° of radius r density $\rho$ in equilibrium at heights o and h. The radius is then calculated from Perrins[31] equation (*c.f. also* Oden[28])—

$$\log \frac{n^\circ}{n} = (\rho - \rho_1) \frac{h\, r^3\, 10^{17}}{1 \cdot 9.}$$

2. *Double Reflecting Condensers.*—The Siedentopf Cardioid[38] and Jentzsch[18] are practically free from spherical aberration and are almost aplanatic. By means of a micrometer eye-piece the area of an illuminated layer of fixed depth—slightly moe than the depth of vision—is determined and the volume calculated. This volume cannot be varied as in the slit or immersion ultra-microscope (*see later*), and the determintions are not so reliable. On the other hand owing to the increased intensity of the illumination it is possible to measure particles which are too small for counting in the slit ultra-microscope, but which can be counted in the new Zsigmondy[61] immersion apparatus. The Jentzsch or Cardioid are particularly suitable for the examination of thread-like bacteria of microscopic length but ultra-microscopic breadth. Such bodies in the slit or immersion ultra-microscope appear as points of light. Siedentopf[39] showed that this was due to illumination from one side only, and that the appearance of such bodies depends on the azimuth of the incident light. Owing to the fact that the illumination in all reflecting condensers is concentric, the complete structure of such bodies is revealed. Since the rays are brought to a sharp focus it is essential that double reflecting condensers should be accurately centred and that the special slide, cell, and cover be " ultra-microscopically clean."

The need for the careful adjustment of these parts after each observation renders the cardioid instrument troublesome for the rapid quantitative examination of a series of sols. This has been recognised by Siedentopf[40] who describes an accessory objective for preliminary qualitative investigations. Jentzsch[23] has designed an ultra-condenser specially suitable for the purpose, the cell of which is provided with inlet and outlet for hydrosols, and if desired with electrical and other fittings. Mention should also be made of the Leitz-Ignatowski[23] Universal condenser, which may be used for both ordinary and dark ground illumination, but the dark field is not so perfect as in the Jentzsch condenser.

The determination of the size of metal hydrosols less than $5\mu\mu$ diameter is best made by the "nuclei" method. It was found that very small particles, $5\mu\mu$ or less (amicrons), which cannot be counted in the slit ultra-microscope, but which give to the field a uniform illumination, can be seen by means of the cardioid condenser. For the determination of their size an indirect method due to Zsigmondy[62] is recommended. It is known that a gold sol prepared under standard conditions by reduction with phosphorus, gives a colloidal solution which contains amicrons only—so small as to be beyond the range of the "slit" ultra-microscope. If some of this solution (containing 5 mgs. of gold per 100 c.c.) be added to a colloidal gold solution which is being prepared by other methods, *e.g.*, formaldehyde or hydrazin) the small amicrons function as nuclei around which the gold present in the second solution builds up, forming a larger particle. Doerinckel and Menz[26] observed that the size of the particles in the resulting solutions depend upon the number of "nuclei" added. Thus, knowing the amount of gold in the nuclear solution it is possible to calculate the size of the amicron nuclei. Good agreement was found within the range of the slit ultra-microscope and the method has been frequently used by Svedberg and Zsigmondy to determine the size of amicrons. Recently Zsigmondy has succeeded in increasing the intensity of the orthogonal illumination in a system similar to the "slit" ultra-microscope so that particles between $5\mu\mu$ and $3\mu\mu$ may now be counted as submicrons. The diameters of such particles as calculated by the "nuclei" method, from observations in the slit ultra-microscope, and as directly observed in the new immersion ultra-microscope agree.

6. *Improved Ultra-Microscopy.*—Other conditions being equal the brightness of the particles seen in the ultra-microscope depends upon the product of the square of the numerical aperture of the condenser and objective. In the slit ultra-microscope it was found necessary[36] to use a condenser of small aperture (·30) and objective of ·75 NA. By using a condenser and objective of high numerical aperture, 1·05 N.A. set orthogonally, Zsigmondy[61] has very considerably increased the intensity of the illumination and the corresponding intensity of the scattered light, so that smaller particles can be detected and measured. Since the focal distance of such a lens system is only 6 mm., it was found necessary to cut away a portion of the front lens and mounting, in order to be able to bring both

objective and condenser near enough to enable the point of focus of the condenser to be observed through the objective set at right angles. The hydrosol to be examined is introduced into the small space between the front lens of condenser and objective, in fact a drop will remain suspended in this position, so that the path of the beam through the solution can be seen. For convenience a small ebonite cup is used to hold the drop in position and this cup is so arranged that fresh hydrosol or water can be rapidly brought into the field by opening a spring clip. The instrument is thus an immersion ultra-microscope with a dark field superior to any other. The illumination is by sunlight or arc lamp and the dimensions of the beam are accurately defined by a special micrometer slit and eye-piece so that particles of gold of $3\mu\mu$ are countable and smaller particles are visible. This apparatus is by far the best for the examination of hydrosols* and no difficulty is experienced when using viscous or jelly-like hydrosols. It has the disadvantage that, unlike the Cardioid or Jentzsch thread-like structures and bacteria are observed as points of light. Observations with this instrument have been reported by Zsigmondy[59]; Zsigmondy and Bachmann[61], and King[20].

7. *Application of Light Absorption.*—The investigations of Garnett[13] and Mie[27] should be referred to but so far insufficient is known of the fundamental relationship to enable the size of the particle to be determined by this means (*c.f.* however Voigt[49], Svedberg, Kruyt[21].

8. *Rayleigh's Formula.*—*See under* Solid Continuous Phase, (b) 1.

9. *Diffusion Constant.*—The Sutherland[42] Einstein[11] equation will be discussed later under gas as continuous phase. The equation has been applied to measurements obtained in highly disperse liquid systems *c.f.* Dabrowski[10], Svedberg, but the method is too tedious to be of practical value.

### III.—*Continuous Phase-Gas* (*Smokes*).

(a) *Microns.*

On account of the rapid Brownian Movement direct microscopic observation is impossible, unless the particles are collected on a microscope slide. Stokes' Law may be applied to gases up to the microscopic limit.

(b) *Sub-Microns.*

The methods are classified as (1) Rayleigh's Law (*see above*, (b) 1); (2) Stokes' Law; (3) Diffusion constant; (4) Ultra-microscopy; (5) Oscillation in alternating field.

2. *Stokes' Law.*—The formula may be used for particles greater than $10^{-4}$ cms. diameter, granules below this size are comparable with the mean free path of the molecules of the gas and Cunningham's[9] correction factor must be applied. For particles $10^{-4}$ cms. the rate

* In 1914, when the author was associated with Zsigmondy in the development of this instrument, only aqueous solutions could be used, since the cement used for fastening the front lens was not chemically resistant. The instrument is now made by R. Winkel, Göttingen.

of fall in air, due to gravity is about 11 cms. per hour, but convection currents interfere with the observation in highly disperse smokes.

3. *Diffusion Constant.*—The value of the diffusion constant D in Sutherland's[42] formula $D = \frac{RT}{N}\frac{1}{3\pi\eta d}$ (where $R = 8{\cdot}316 \times 10^7$ $N = 606 \times 10^{23}$) may be substituted in the Einstein equation $x = \sqrt{2Dt}$ for the displacement x due to Brownian Movement. This gives a simplified equation $d = 4{\cdot}7 \times 10^{-11}\ t/x^2$ for calculating the diameter d of a particle in air as continuous phase at room temperature (20° C.) when the mean displacement x in time t is measured. This displacement was recorded photographically by De Broglie[3], but such records are reliable only if a photographic plate moving at a known rate be used. Owing to the impossibility of excluding convection effects this method is not recommended for measuring the size of granules in highly disperse gaseous systems.

4. *Ultra-Microscopy.*—Smokes are conveniently observed in the Jentzsch or "slit" ultra-microscope, but not in any of the others. Precaution should be taken to prevent disturbance due to convection and heating by using a heat filter (ferrous-ammonium sulphate solution 1 : 5) in the path of the beam.

5. *Oscillation in an Alternating Electric Field.*—If the particles are charged, they will move in an electric field, according to Stokes' Law, with a uniform mean velocity.

$$V = \frac{Xe}{3\pi\eta d}$$

where X is the field in volts per centimetre and e the electronic charge (*c.f.* Hevesy[16]). By measuring the velocity and the field the diameter of any individual particle is determined. This method has recently been applied by Wells and Gerke[52] to the examination of smokes. By means of a rotating commutator the particles were caused to oscillate, and their motion was observed, either photographically or by means of a micrometer eye-piece, in a modified Zsigmondy ultra-microscope constructed for this purpose. Since the motion due to convection was perpendicular to the oscillation a zig-zag line was obtained. It was thus possible to measure the oscillation amplitude which, multiplied by the frequency of the field reversal gave the velocity. By varying the field and determining the corresponding velocities good agreement was obtained for the diameter of a tobacco smoke particle ($2{\cdot}73 \times 10^{-5}$ cms.). The method can be used for the measurement of the size of individual particles in a non-uniform disperse phase. This represents a distinct step forward. von Weimarn proposes to construct an ultra-microscope with quartz or fluorite lens and to use ultra-violet light, which by reason of its short wave length will increase the intensity of scattered light. With such an instrument, using the photographic plate method of Wells and Gerke[52], it should be possible to make still further progress into the realms bordering on the molecular.

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# THE SOLUBILITY, RATE OF ABSORPTION AND OF EVOLUTION OF GASES, AS INFLUENCED BY COLLOIDS, WITH SPECIAL REFERENCE TO PHYSIOLOGY AND BREWING.

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Although the conditions governing the equilibrium in the simple gas-liquid and gas-solid systems, have received a considerable amount of attention both theoretically[28] and experimentally[24] no satisfactory explanation has yet been given of the mechanism of the process[58]. It is not surprising, therefore, to find that comparatively little systematic work has been done on the more intricate problem of gas distribution in colloidal solutions, although it is with such solutions that many of the problems of biology, brewing, botany, sanitation, and agriculture are chiefly concerned. For the purpose of this report the experimental investigation will be considered under :—(1) gas solubility in colloidal solutions; (2) rate of evolution (effervescence); (3) rate of solution (aeration).

## I.—*Solubility.*

The well-known Ostwald* co-efficient of solubility gives the ratio of the concentration of the gas in the liquid and gaseous phase $C_l/C_g = \lambda$ (solubility) and is an alternative expression of Henry's Law. This law, as Findlay[15, 16, 17], has shown, is valid for solution of the common gases in water and aqueous solutions of salts and non-electrolytes, at 25° C., and over a pressure range of 250 mm. to 1,400 mm. of mercury. Cassuto[10], working between one and ten atmospheres, and, more recently, Sander[49], at pressures up to 160 atmospheres observed that, at high pressures, the solubility ($\lambda$) decreased slightly with increasing pressure.

At such pressures (2,500 lbs. per square inch) the gas concentration in the liquid phase is high, and the observed departure from Henry's Law is presumably closely connected with the compressibility of the concentrated gas solution (*c.f.* Ritzel[48]). Biologists often express solubility in terms of Bunsen's coefficient of absorption—the quantity of gas in cubic centimetres at N.T.P. which is absorbed by unit volume of the liquid at 760 mm. pressure. This coefficient has not proved so satisfactory as the solubility coefficient of Ostwald, and Sackur and Stern[50] propose to refer the gas absorbed to unit mass of the liquid. Stern[55] has recently determined the solubility and absorption co-efficients for solutions of carbon-dioxide in aliphatic alcohols, and found that Henry's Law held good to within one per cent., and that the solubility coefficient was constant over a much wider range of pressures than the modified Bunsen coefficient (*c.f. also* Drucker[12]).

### (a) *Physiological Aspect.*

The difficulties which physiologists have encountered in explaining the transport of oxygen and carbon-dioxide by blood have been

* In a paper published in 1877 (Hufner Wied Ann, 1633) it is suggested that instead of employing Bunsen's coefficient, solubility should be expressed as " das Verhältnis des adsorbierenden Flüssigkeits volumens zum absorbierten gas Volumen " (Drucker).

discussed by Professor W. M. Bayliss in the Second Report of Colloidal Chemistry, 1918, p. 151. The study of colloidal chemistry has thrown new light upon the problem of the abnormal solubility of these gases in blood. Findlay and Harby[14] (1908) suggested that the effect is due, partly to absorption on the surface of the disperse phase, and partly to ordinary chemical combination. The accepted view was that absorption of oxygen by blood was due to the formation of a compound of oxygen with the hæmoglobin; and this view has recently received the support of Barcroft[4]. According to Peters[44]—on the basis of the iron content of hæmoglobin—one molecule of hæmoglobin combines with one molecule of oxygen, but the total quantity of oxygen absorbed, for one gram of iron, varies according to the nature of the blood, being 280 c.c. to 401 c.c. for pig's blood and 320 c.c. to 468 c.c. for dog's blood. This considerable variation must be due to the difference in the chemical or physical nature of the hæmoglobin and not to any great extent to variation in the plasma, for the total amount absorbed by centrifuged plasma of dog's blood is only 12·6 c.c., whereas the variation in total gas absorbed is 40 c.c. to 70 c.c. In order to investigate the influence of colloidal hæmoglobin on the solubility, Findlay[15–21] and co-workers carried out a series of systematic investigations on the influence of colloids and fine suspensions on the gas solubility. The specific effect due to the colloid was investigated by studying the influence of concentration and pressure on the solubility coefficient. The following are typical of the 17 colloids used :—ferric hydroxide, gelatin, starch, ox blood, hæmoglobin, peptone. Carbon-dioxide and nitrous oxide were used, and it was found that, for both gases, at pressures below atmospheric, the solubility ($\lambda$) is sometimes less, sometimes more, than in water, it always falls with increasing pressure, and passing through a minimum, rises again slightly.

The pressure at which the minimum occurs is practically constant for all concentrations of a particular sol, but varies for different solutions. It has been tentatively suggested by Findlay and Creighton[16] that this unique behaviour is due to gas solubility in the disperse phase and since the solubility then no longer follows Henry's Law, it must be assumed that gas polymerises in this phase. For the upward trend of the curve the increased solubility can be satisfactorily interpreted in terms of the absorption law. $C^4_2/C_1 =$ constant (*e.g.*, serum albumen, charcoal, suspensions).

It is well known that the solubility of gases in salt solutions decreases with increasing salt concentration[24]—provided there is no chemical reaction. About 20 aqueous solutions of non-electrolytes have been studied, and in three only, Quinol, Resorcinol[60], and Aniline[16] is the solubility of carbon-dioxide greater than in water. These exceptions are no doubt due to chemical combination of the solute with the gas.

In considering the influence of the concentration of colloids on solubility, distinction must be drawn between suspensoids and emulsoids. In physiological and technical chemistry, suspensoids occur but seldom. Geffcken[24] and Findlay[16] have both found that the solubility ($\lambda$) of carbon-dioxide in arsenious sulphide sols, is less than in water, and the latter has observed that it is constant for

all pressures, furthermore the hydrogen[17] solubility in silver hydrosol was indistinguishable from that in water. Very different is the influence of emulsion colloids on the gas solubility, which is often considerably influenced by the concentration of the disperse phase, and especially is this so with serum albumen, egg albumen, starch, and dextrin, in which the solubility of carbon-dioxide[15], nitrous oxide[20], and hydrogen[17] is less than in water. Thus the behaviour is comparable with that of the non-electrolytes and salt solutions, and in fact provided adsorption and chemical combination do not interfere, *collodidal solutions in general diminish the gas solubility.* Thus gelatine, glycogen, ferric hydroxide, ox blood and serum diminish the solubility of nitrous oxide[16] at atmospheric pressure, so also hydrogen in gelatine, nitrogen in blood and serum, and carbon monoxide in serum[15] have a lower solubility than the corresponding gas in water.

For each system at and above a definite pressure there is evidence of adsorption, this adsorption effect being greatest for egg and serum albumen and least for gelatine and starch. Very different, however, is the behaviour of a gas which is known to act chemically with the disperse phase in solution. In such systems as carbon-dioxide in methyl orange[17], hæmoglobin, ox blood, and serum, and carbon-monoxide and oxygen in ox blood and serum[15] the gas solubility ($\lambda$) is very considerably increased, and within the range of the pressure investigated (to 1500 mm. of mercury) the solubility decreases with the pressure and the curves show no evidence of adsorption. Judging from solubility pressure measurements gelatine[19], ferric hydroxide[16], peptone[17], and propeptone[17], react chemically with carbon-dioxide and evidence from other sources confirms this view (*c.f.* Stocks[56], Luther[35]). These observations, therefore, support the chemical theory of oxygen and carbonmonoxide absorption by blood and clearly indicate that the absorption of carbon-dioxide must also be considered as in part due to chemical combination. This view of the carbon-dioxide solubility is supported by Harnack[26], Tissot[59], and more recently by Buckmaster[6] (*c.f. also* Boycott[7]). Mention should be made here, however, of the paper by Christiansen[11] and co-workers on the reciprocal solubility of these gases in blood in which the authors support the adsorption theory.

(b) *Botanical Aspect.*

The question of the assimilation of carbon-dioxide by plants has been shown by Willstätter[63] to depend upon the nature of the colloidal chlorophyll, and some experiments have shown that, whereas chlorophyll in organic solvents behaves as an electrolyte (*c.f.* Kremann[29]) and does not increase the gas solubility, the same chlorophyll in aqueous solution produces an hydrosol which absorbs much more gas " than other colloidal solutions."

(c) *General Application.*

(1) Wolman and Emslow[64] :—Chlorination of turbid river water.
(2) D. Berthelot[5] and R. Trannoy :—Absorbent power of dry and

moist earth with respect to chlorine gas. (3) Swanson[57] and Hulett :— Estimation of gases in effluents by partition between vacuum and liquid—assumption that Henry's Law holds true for such solutions.

(d) *Application to Brewing.*

In the brewing industry it has long been recognised that a knowledge of the carbon-dioxide equilibrium is of the first importance in connection with the sprakling quality, persistency of head and palatability of beer. After Langer[31] and Schultze's experiments it was for a long time thought that the solubility of carbon-dioxide in beer was greater than the solubility in a corresponding water-alcohol solution. Prior[46], modifying the method of investigation, considered that increased absorption was due to presence of phosphates. The mean phosphate content of beer, however, is about ·07 per cent.; insufficient to explain any considerable increase in carbon-dioxide solubility. The assumption that an ester of carbon-dioxide and alcohol is formed, has been shown by Mohr[39] to be without foundation as also was the suggested combination with proteids. Mohr concluded that the gas was merely held in suspension to an extent determined by the viscosity. On the basis of Langer's experimental data, Emslander[13] and Freundlich, considered that the increased solubility was due to *adsorption* of the gas by the colloids—chiefly dextrin and albuminoids. These colloids have each been found to lower the solubility of carbon-dioxide in water; and alcohol also lowers the solubility (Müller[40]). It is not surprising therefore that Findlay and Shen[18] found for wort and different grades of beer that, contrary to the usually accepted view, the carbon-dioxide solubility was considerably less than for water, and independent of pressure. Increase in alcohol content, with corresponding increase in total colloids,* was shown, also, to decrease the solubility, and that even allowing for the alcohol, the solubility was much less than in water. It is evident that the method used by the earlier investigators gave the total amount of carbon-dioxide in a beer which was supersaturated to an unknown degree. Distinction must therefore be drawn between true solubility, and degree of supersaturation, and to understand the problem better the second aspect of gas equilibrium must be considered, namely :—

## II.—*Rate of Evolution of Gas.*

It is well known, although not always sufficiently well recognised, that gas supersaturation readily occurs in aqueous salt solutions (Lamplough[32]), and in ordinary brewing practice during fermentation in cask, the beer becomes supersaturated. It was shown by Findlay and King[22] that certain colloidal solutions supersaturated with carbon-dioxide remain quiescent, sometimes over a period of 20 minutes. In this condition of metastability the solution is exceedingly sensitive, a very slight mechancial shock being sufficient to cause gas evolution (*c.f.* Young[65]). Such quiescence only occurs if scrupulous care is taken in the cleaning of the apparatus and filtration of the solutions

* According to Marc colloids are proportional to total solids present in beers.

used (Veley[62]). The period of quiescence is followed by periodic evolution of gas, and the duration of the period is, perhaps, a measure of the rate of growth and number of gaseous nuclei formed in the liquid. No quiescence was observed with solutions of peptone and ferric hydroxide, but after an initial rapid effervescence the process went on as in the case of the other solutions. An important contribution to our knowledge of the law governing the rate of escape of gases from solution was made by Carlson[9] (1911), who passed an indifferent gas over a well-stirred solution of oxygen in *water*. This method of investigation (Bohr[8]) enables the results obtained, as Meyer[83] pointed out, to be interpreted in the light of the Nernst[42] diffusion theory. Perman[45] and later Steele[54] showed that the rate of removal of carbon-dioxide by a stream of air, was proportional to the concentration of the gas in solution. Both the apparatus employed and the method of interpreting results are well suited for the investigation of colloidal solutions. In the only investigation of this nature which has been reported, Findlay and King[22] used mechanical shaking and supersaturated solutions of carbon dioxide (saturated at two atmospheres and reduced to one). Experimental conditions so obtained are more in accordance with those encountered in brewing, and it was shown that the gas effervescence is considerably influenced by both the quantity and nature of the disperse phase.

Using water as a standard of reference the degree of supersaturation was proportional to the rate of evolution* and inversely proportional to the coefficient k in the equation—

$$\text{Velocity} = k \times (\text{degree of supersaturation}).$$

By plotting the values of velocity coefficient against degree of supersaturation a means of representing distinctly the characteristic behaviour of colloids is obtained. Hugo Muller[41] observed that freshly carbonated water loses its gas more readily than a solution which has stood. This was not confirmed, for all observations on water k is almost constant and directly proportional to degree of supersaturation.

There is a much more rapid evolution of gas initially from solutions of gelatine, peptone, ferric hydroxide, and agar, than from water solutions of potassium chloride, dextrin, starch and platinum sol (dilute), in fact, a ·05 per cent. gelatine sol effervesces as rapidly as a 3 per cent. dextrin or starch solution and a little more than half as rapidly as a ·7 per cent. peptone sol. Towards the end of the effervescence, *i.e.*, as the degree of supersaturation diminishes, in the gelatine and agar solutions, the velocity coefficient increases —the more so the greater the concentration. But there is a marked falling off in the value of the coefficient for solutions of dextrin, starch, peptone, ferric hydroxide and suspensions of charcoal. Such decrease is attributed to the slow outward diffusion of the gas dissolved in the disperse phase. With carbon the effect was observed *only* when the suspension was kept in contact with the gas for a

* That the logarithmic law holds true for rate of evolution from supersaturated solutions is confirmed by calculations from the Pressure recovery curves of Patten and Mains[43] for carbonated water.

prolonged period. This slow outward diffusion from solid solution is the counterpart of the phenomenon observed when the initial taking up of the gas is followed by a period of very slow absorption. The same behaviour was observed by Lefebure[33] (1914) for the rate at which gases are taken up by celluloid, and a similar explanation is given. The comparatively slow saturation of beer containing high proportion of solids is, without doubt, to be interpreted as evidence of solution of the gas in the disperse phase, the rate of which is directly proportional to the rate of diffusion.

Practically nothing is known of the mechanism of this solution in the solid phase, and it is instructive to compare the phenomena observed by Findlay and King[22] with the results obtained by Anderson[1] who investigated the rate of elimination of water vapour from silicic acid gels[65].

Anderson showed that the rate depends upon the capillary structure of the gel and towards the end of the dehydration the rate is influenced by the same phenomena which is responsible for a section of the Van Bemmelen[61] curve. Anderson's results recalculated in terms of the velocity coefficient used by Findlay and King yield a curve of the same form as that obtained by the latter for starch, dextrin, and suspensions of charcoal. The influence in the Van Bemmelen and Anderson curve is considered to indicate solid solution of the gas in the walls of the capillaries (Zsigmondy[65]). The slow evolution of gas from solutions of starch, peptone, and dextrin is obviously of considerable importance in connection with the palatability and sparkling quality of beverages, and if, as it appears, this depends upon the slow diffusion outward from the disperse phase, every facility must be afforded, during carbonation, for the gas to dissolve in that phase. In fact the beer should, as Langer[30] has shown by practical tests, contain a high proportion of residual extracts, and be carbonated at low temperature. The assumption by Siegfried[52] of the formation of a carbamic acid which at the higher temperature of the palate gives free carbon dioxide would seem to be unnecessary. The formation of head is governed by the rate of effervescence, the increase being greater, the greater the concentration of colloids, within limits obviously determined by viscosity. More important, however, is the absence of substances tending to reduce the surface tension (Bau[3]), and according to Ihnen[27] under similar conditions those beers rich in dextrins retain the foam best.

When the complicated phenomena of gas solubility in colloidal solutions is better understood, it will no doubt be found that much of the conflicting evidence as to the effect of colloids will be explained, simply, as due to alteration in the physical condition of the particular colloid. It has long been known that gelatine solutions if repeatedly heated above 60° C. lose their power of jellying when cooled. The experiments of Menz[37], Ganett[25], von Schroeder[51], and more recently, Smith[53], have shown that both an irreversible change (decomposition ?) and a reversible change gel sol takes place. At temperatures above 35° C. sol is stable, the gel form being stable below 15° C. When a solution is cooled between these two temperatures the change sol so gel does not take place at once but the equilibrium depends on

temperature and time during which the solute is heated, and on the rate of cooling of the solution. Such variations must be taken into account and carefully controlled, since it has been shown that the physical condition of both gelatine and starch has a very considerable effect on the rate of escape of gas from solution, in fact the determination of gas evolution provides a means of closely following the changes indicated above, and of investigating the nature and history of a particular gelatine. (For details, *see* Findlay and King[23], Part II.)

## III.—*Rate of Solution.*

Except for incidental observations by Findlay and co-workers and by Geffcken, no investigation on this question appears to have been reported. A bibliography of work published on the rate of solution *in water* will be found under Papers 2, 9, 34, 38, 43, 47, 64.

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## THE ELECTRICAL CHARGE ON COLLOIDS.

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The origin of the electrical charge on colloids is still a matter of uncertainty, although it is possible that the charges may not always arise from the same cause. It has been common practice for writers to shelve the question by assuming that a sufficiently satisfactory answer is given by Coehn's empirical law that " a substance of higher dielectric constant charges itself positively when it comes in contact with a substance of smaller dielectric constant." Even if the statement of this law were true, it would not constitute an explanation since it tells nothing regarding the manner of bringing about the charging.

Taylor has suggested the possibility of the charge arising from the colloid surface being more impermeable to certain ions than to others. He found that a membrane of aluminum hydroxide is formed by the interaction of aluminum salts and ammonia which is permeable to hydrion, but impermeable to hydroxidion, even a large E.M.F. failing to drive hydroxide ions across such a film. Thus, when alumina is suspended in water, the hydrion dissolves in or diffuses into it, leaving the hydroxidion at the surface, and the particles become positively charged. This will also explain the alteration of the charge on albumen by acids and alkalis, if it may be assumed that hydrogen and hydroxide ions are equally soluble (or diffusible) in albumen. In such a case the concentration of either ion in the albumen would vary directly as its concentration in the solution This explains why albumen possesses no charge in neutral solution

and why the positive charge increases with increasing acidity and the negative charge with increasing alkalinity. However, Taylor admits that these explanations are not necessarily correct, because they fit the facts and even suggests that adsorption, rather than differential diffusion, is responsible for the charge.

The great majority of opinion regarding the origin of the charge seems to be included in the following possibilities; that the charge results from the selective adsorption of ions at the surface of the colloid; that it is due to the ionization of foreign substances incorporated in the surface of the particles; or to the ionization of the colloid itself.

In his recent book, Burton gives an interesting discussion of the subject. In hydrosols of the oxidizable metals, the particles are positively charged, while in hydrosols of the non-oxidizable metals, the particles are negatively charged. Hardy explained this on the assumption that the charge is due to a reaction between the metal and water at the moment of formation of the hydrosol. In the case of the oxidizable metals, ionizable hydroxides are formed; in the case of the non-oxidizable metals, ionizable hydrides. The particles, however, are so comparatively large that the greater portion of the metal compound has the properties of matter in mass and ionization takes place only at the surface of the particles. Burton has confirmed this view by experiments with methyl and ethyl alcohols, which have easily replaceable OH groups. He was unsuccessful in repeated attempts to prepare alcosols of platinum, silver, and gold, but succeeded in preparing alcosols of the oxidizable metals. On the other hand, when platinum, gold, and silver wires were sparked under ethyl malonate, which has a replaceable hydrogen, very stable sols were obtained, in which the particles were negatively charged; but sols of the oxidizable metals could not be obtained with ethyl malonate. Burton's own view is that the charges on the particles are due, in the case of the Bredig metal sols, to the ionization of a layer of hydroxide or hydride on the surface of the particles. Duclaux believes that the charge always arises from the dissociation of a portion of extraneous substance retained by the particles from the reacting media and he has shown that there is always a trace of $FeCl_3$ in $Fe(OH)^3$ sols.

Zsigmondy admits that in special cases the charge is due to the ionization of the colloid itself, for example, where an ionizable substance has molecules so large as to give it the properties of a colloid. He objects to the idea of the formation of chemical compounds in all cases on the ground that it would entail "the inclusion in the category of chemical compounds of a large number of badly defined bodies, and load chemistry with much useless ballast." He prefers explaining such reactions on the basis of adsorption of ions. The acceptance of Langmuir's explanation of adsorption as a chemical phenomenon would reduce Zsigmondy's objection to one of terminology.

Among the more recent papers dealing with colloidal metallic hydroxides may be mentioned that of Pauli and Matula, who confirm Duclaux's belief concerning colloidal $Fe(OH)_3$. Kimura regards the charge as due to simple ionization of the hydroxide, the extent of which is determined by a balancing of the forces causing ionization

and the attractive forces acting between the positively charged particles and the hydroxide ions. But Powis produced negatively charged colloidal ferric hydroxide by adding a sol of the common type to a dilute solution of sodium hydroxide. He considered the change in sign of the charge to be due to the adsorption of hydroxidion.

No reliable method has yet been devised for determining the absolute value of the electrical charge on a colloidal particle. From Burton's data, Lewis made an extremely rough calculation of $8 \times 10^{-5}$ electrostatic units for a platinum particle. Powis calculated a value of about $2 \times 10^{-7}$ for a coarse silver particle. Upon the assumption of the existence of the Helmholtz double-layer at the surface of colloidal particles, the difference of potential between the disperse phase and the medium has been calculated. The voltages found lie almost entirely between $-0{\cdot}07$ and $+0{\cdot}07$. The results of Ellis and of Powis for oil emulsions indicate that for a stable emulsion the absolute value of this voltage must be greater than $0{\cdot}03$. Between the values $-0{\cdot}03$ and $+0{\cdot}03$, complete coagulation occurs, but at a velocity apparently independent of the voltage.

Wilson has shown that the electrical charge on the surface of colloidal particle must cause an unequal distribution of ions between the surface layer of solution surrounding the particles and the bulk of solution, which would, in turn, result in a difference of potential between the two phases. A very important conclusion of this work is that the addition of an electrolyte to a sol, provided no chemical changes follow, must result in a lowering of the absolute value for the potential difference between the two phases, even though there may be no change in the magnitude of the electrical charge on the colloid itself. This is considered to be the explanation of the precipitation of suspensoids by addition of salt.

This subject is so closely allied to that of electrical endosmose that the report compiled by Briggs (Second Report, p. 26) should be consulted.

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## IMBIBITION OF GELS—PART I.

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One of the commonest methods of demonstrating what is meant by imbibition is to immerse a thin sheet of ordinary gelatin in water. In less than an hour the gelatin will be found to have become much swollen by absorbing, or *imbibing* water. After the first hour, the rate of swelling noticeably decreases, and the volume papers to approach a definite limit. The amount of water taken up can be determined by weighing the gelatin before and after swelling. The absorbed water behaves much as though it were dissolved in the gelatin, and it can be removed by washing the gelatin with absolute alcohol. As the water is removed, the volume of the gelatin diminishes, approaching its volume before swelling. During imbibition heat is evolved, which has often been referred to as heat of swelling. Probably this is responsible for the repeated statement that the application of heat will repress the swelling of gels. On the contrary rise of temperature causes greater swelling, which seems to indicate that the liberation of heat is not due to swelling, but to some other cause, which the writer believes to be chemical combination between the gelatin and a small portion of the absorbed water. Procter has shown that the degree of swelling is also dependent upon the previous history of the gelatin. He prepared three solutions containing 5 per cent., 10 per cent., and 20 per cent. respectively of gelatin and allowed them to set. He then dried the jellies and, after weighing, allowed them to soak in water for seven days. The sample with the

greatest volume at time of setting absorbed 14·6 times its weight of water, the second sample, 7·7; and the sample with smallest setting volume only 5·8 times its weight of water.

Gelatin swells to a much greater extent in dilute acid solutions than in water. The parts of solution absorbed by one part of a certain sample of gelatin, at 18°, were in pure water 8, in 0·006 N HCl 42, in 0·05 N HCl 28, in 0·3 N HCl only 17. Stronger solutions of the acid caused the gelatin to soften and finally dissolve. This action appears to be independent of the swelling phenomenon, and at higher temperatures becomes more marked, even with lesser concentrations of acid. By plotting the amount of swelling against the concentration of acid up to 0·3 N, a curve with a maximum is obtained, the explanation of which has given rise to several theories, which will be treated later.

The most extensive investigation of the hydrochloric acid gelatin equilibrium seems to have been made by Procter, who showed that the concentration of free acid is always less in the solution absorbed by the gelatin than in the remaining external solution, and that the sum of the amounts of free acid in both these solutions is less than the amount in the solution before the introduction of the gelatin. He attributes this difference to chemical combination between the gelatin and some of the acid and regards the product as a hydrolyzable, but highly ionizable chloride of gelatin. This agrees with the electrometric determinations of Manabe and Matula, who found that in certain hydrochloric acid solutions of gelatin nearly all hydrogen ions were bound by the protein and nearly all chloride ions were free. They examined acid solutions of serum albumin similarly and regarded the behaviour of both proteins as that of weak bases forming hydrolyzable salts.

Gelatin swells likewise in solutions of other acids, but not to the same extent as in HCl, nor does the point of maximum occur at exactly the same concentration of either total acid or hydrogen ion. With strong acids the maximum in the swelling curve is very pronounced, becoming less so with weaker acids. With acetic acid the maximum is hardly reached at concentrations so great as to cause solution of the gelatin. Extremely weak acids like boric produce very little swelling.

If sodium chloride, or other neutral salt, be added to acid-swollen gelatin, the latter contracts and gives up the solution it had absorbed to an extent depending upon the concentration of added salt. If the solution be saturated with salt, the gelatin shrinks to a horny mass. Fischer found that even non-electrolytes, such as sugars, produce this repression of swelling, although not nearly to the same extent as salts. Repression is produced by the acid itself when present in concentrations greater than that required to produce maximum swelling.

Experiments dealing with the swelling of gelatin in alkalis are generally not so satisfactory as those with acids, because of the more powerful solvent action of alkalis on the swollen gelatin. Nevertheless, by using only very dilute solutions at low temperatures, sufficient data have been collected to show that alkaline swelling is of the same

general nature as acid swelling. The swelling increases with increasing concentration of alkali to a maximum and then falls until such concentration is reached that the gelatin softens and dissolves. Swelling is repressed, here too, by addition of neutral salts.

While neutral salts are capable of repressing the swelling of gelatin in acids and alkalis, it must not be overlooked that they are also capable of producing swelling. Procter found that, with increasing concentrations of sodium chloride, gelatin swells to a maximum and then contracts steadily until the solution is saturated. The swelling was not so marked as in the case of acids, however, the gelatin taking up a maximum of only about 17 times its weight of water as compared to three times this amount with HCl. He also noted that the gelatin removes some of the salt from solution, suggesting combination, but that the addition of HCl again liberates this salt and causes the salt to become more concentrated in the external solution than in the solution absorbed.

Loeb has done some work on neutral salts that should be mentioned here. In each of a series of experiments he placed two grams of finely powdered gelatin into a cylindrical funnel, the powder being held in the cylinder by a circular piece of filter paper. One sample was perfused six times in succession with 25 c c. of distilled water and the amount of swelling noted, which was taken as the height in millimetres to which the gelatin rose in the cylinder; this sample was taken as the standard. Another sample was perfused twice with 25 c.c. of M/8 NaCl, and then four times with 25 c.c. of distilled water; the swelling here was several hundred per cent. greater than that of the standard. Still another sample was perfused six times in succession with 25 c.c. of M/8 NaCl; it did not swell to any greater extent than the standard. Loeb attributes these results to a chemical combination between the gelatin and salt, a highly ionizable sodium gelatinate being formed. In the third experiment, much swelling was prevented by the excess of salt present; when this was washed away, as in the second experiment, the gelatin swelled to a much greater extent than in pure water. He confirmed this view by showing that, when placed in an electric field, gelatin which has been treated with NaCl migrates to the anode. A sample first perfused with calcium chloride solution and then with distilled water showed very little more swelling than the standard. He accounts for this by saying that the calcium gelatinate formed is only very slightly ionizable.

Collagen, fibrin, and other proteins behave much like gelatin when immersed in solutions of acids, alkalis, or salts, and are probably subject to the same general laws. Other examples of imbibition are the swelling of agar-agar, gums, and cellulose in water and the swelling of rubber in organic solvents. It would take volumes to mention all of the work done on this subject.

Numerous attempts have been made to explain the molecular mechanism of imbibition, particular attention being paid to the explanation of the peculiar swelling curve. Most of these, however, have been guilty of drawing largely upon the imagination for something that would agree qualitatively with the experimental data

without regard for lack of grounds for the assumptions involved, Several of these still survive because, while they cannot be proved, they are not of a nature to be easily disproved. It will probably be sufficient to outline two of the more recent ones.

Perhaps it would be unfair to consider Fischer's theory of imbibition as attempting to give an explanation of the molecular mechanism of the phenomenon. He regards gelatin as a substance capable of existing in different degrees of association or polymerisation; in other words, the particles of gelatin may vary greatly in size, dependent upon conditions to which they are subjected. Thus rise of temperature or increase in concentration of acid or alkali, causes the particles to become smaller in size, the change being reversible. The particles are assumed to be capable of becoming most heavily hydrated, that is, of absorbing most water, when they have a medium diameter. The particles of neutral gelatin are large and capable of absorbing comparatively little water. Increasing the concentration of acid decreases the size of the particles, making them capable of absorbing more water, and the gelatin swells until the size of particle most readily hydrated is reached. As the particles become still smaller, the swelling becomes less until finally the particles become so small that the gelatin apparently goes into solution.

The theory of Tolman and Stearn assumes that, because of their amphoteric nature, protein colloids have marked tendencies to adsorb hydrion from acid solutions and hydroxidion from alkaline ones. In a solution of a strong acid, the adsorbed hydrogen ions, together with a corresponding number of anions, form a " double layer " on the walls of the pockets or pores in the interior of the gel, and this leads to swelling and imbibition of water by electrostatic repulsion. The addition of neutral salt or excess of strong acid to such a swollen colloid will furnish ions in the interior of the pockets which will tend to arrange themselves so as to neutralise the electrical fields of the adsorbed layer and thus being about a reduction of the swelling. The addition of a neutral salt to the acid solution tends to neutralise the electrical field of the adsorbed acid, making it easier for more acid to get to the surface of the pockets, thus leading to increased adsorption. Polyvalent ions are more effective than univalent ions in reducing swelling because, while taking up no more room than univalent ions, they are twice as effective in neutralising an existing electrical field.

In contrast to these stands the theory originated by Procter and developed by him in collaboration with his pupils. By very extensive investigations with gelatin and aqueous solutions of acids and salts, he succeeded in finding quantitative relationships between several of the variable factors involved. Once a foothold was gained in the form of an equation, it was found possible to make big advances merely by an application of mathematics. Procter built up his theory from experimental data; more recently J. A. and W. H. Wilson worked in the opposite direction by purely mathematical reasoning from the assumption of the existence of a certain hypothetical substance and calculated what results Procter should have found experimentally.

All of their calculated curves coincided completely with Proctor's experimental ones, and for this reason the writer considers the essential part of the theory as proved. The importance of the subject warrants our giving a review of the mathematical deductions, which include an adequate explanation of Procter's theory.

Consider the purely hypothetical substance $G$ which is a colloid jelly completely permeable to water and all dissolved electrolytes, is elastic and under all conditions under consideration follows Hooke's law, and which combines chemically with the positive, but not the negative ion of the electrolyte $MN$, according to the equation—

$$[G] \times [M^+] = K[GM^+] \qquad (1)$$

In other words, the compound $GMN$ is completely ionized into $GM^+$ and $N^-$. The brackets indicate that concentration is meant and all concentrations are in moles per litre. The electrolyte $MN$ is also considered totally ionized.

Now take one millimole of $G$ and immerse it in an aqueous solution of $MN$. The solution penetrates $G$, which thereupon combines with some of the positive ions, removing them from solution, and consequently the solution within the jelly will have a greater concentration of $N^-$ than of $M^+$, while in the external solution $[M^+]$ is necessarily equal to $[N^-]$. The solution thus becomes separated into two phases, that within and that surrounding the jelly, and the ions of one phase must finally reach equilibrium with those of the other phase.

At equilibrium, in the external solution, let—

$$x = [M^+] = [N^-]$$

and in the jelly phase let—

$$y = [M^+]$$

and—

$$z = [GM^+]$$

whence—

$$[N^-] = y + z.$$

The relation existing between the concentrations of diffusible ions of the two phases at equilibrium can be derived from the consideration of the transfer of an infinitesimally small amount, $dn$ moles, of $M^+$ and $N^-$ from the outer solution to the jelly phase, in which case, since no work is done—

$$dnRT \log x/y + dnRT \log x/(y + z) = 0,$$

whence—

$$x^2 = y(y + z). \qquad (2)$$

But in this equation, the product of *equals* is equated to the product of *unequals*, from which it follows that the sum of those unequals is greater than the sum of the equals, or—

$$2y + z > 2x.$$

This is a mathematical proof that the concentration of diffusible ions of the jelly phase is greater than that of the external solution, and makes possible the derivation of a second equation involving $e$,

which is defined as the excess of concentration of diffusible ions of the jelly phase over that of the external solution—

$$2x + e = 2y + z. \tag{3}$$

Since $[N^-]$ is greater in the jelly than in the surrounding solution, the negative ions of the colloid compound will tend to diffuse outward into the external solution, but this they cannot do without dragging their colloid cations with them. On the other hand, the cohesive forces of the elastic jelly will resist this outward pull, the quantitative measure of which is $e$, and according to Hooke's law—

$$e = CV \tag{4}$$

where $C$ is a constant and $V$ the increase in volume in cubic centimeters of one millimole of the colloid.

Now, since we have taken unit quantity of the substance $G$—

$$[G] + [GM^+] = 1/(V + a)$$

or—

$$[G] = 1/(V + a) - z \tag{5}$$

where $a$ is, not the initial volume of the colloid, but the free space within the jelly before swelling through which the ions may pass. For our hypothetical substance, we may consider the limiting case where the value of $a$ is zero, in which case, from (1) and (5) we get—

$$(1/V - z)y = Kz \tag{6}$$

and from (2) and (3)—

$$z = e + 2\sqrt{ey}$$

or—

$$z = CV + 2\sqrt{CV}y \tag{7}$$

From (6) and (7)—

$$V(K + y)(CV + 2\sqrt{CV}y) - y = 0 \tag{8}$$

where the only variables are $V$ and $y$. Now we have only to know the values for the two constants, $K$ and $C$, to plot the curve for any variable in terms of any other value. For example, by giving $y$ a definite value, we can calculate $V$ from (8). Knowing $y$ and $V$, we can calculate $z$ from (7) and with $y$ and $z$, we can calculate $x$ from (2), while $e$ is obtained directly from (4).

If any values for $K$ and $C$ be substituted, the resulting relations will be found to be of the same general nature as are obtained with any proteins in acid solutions, but values of $K$ and $C$ for gelatin have been determined. By means of the hydrogen electrode, Procter and Wilson found the value $K = 1{\cdot}5 \times 10^{-4}$ for gelatin and HCl, while their experimental value for $C$ at 18° was $3 \times 10^{-4}$. The whole series of curves for these values of the gelatin constants has been plotted, and appears in the *Journal of the American Leather Chemists' Association* for 1918, pages 184 and 185, which should be consulted. Procter's experimental determinations are included in the same figures, and it will be seen that better agreement could not be obtained if the curves were drawn from his data.

Since, theoretically, the calculated curves should not coincide absolutely with the experimental ones for gelatin and HCl, it is interesting to note why no appreciable discrepancies were found.

That the quantity $a$, defined as the free space within the unswollen jelly, has a measurable value for gelatin is suggested by the fact that the volume of the swollen jelly is slightly less than the sum of the volumes of the gelatin and absorbed water before swelling. But the values for $V$ are generally so much greater than the total volume of the gelatin before swelling that any error due to neglecting $a$ would be insignificant. Appreciable errors might have resulted from the assumption of total ionization of the electrolyte, were it not for the fact that the rates of change of the slopes of the curves are greatest for concentrations of HCl less than 0·01 N.

In order to apply the theory to weak acids, it is necessary to include the equation which defines the ionization constant of the acid. Procter and Wilson have derived equations which explain the action of salt in repressing the swelling of gelatin in acid solutions; for these and others dealing with polybasic acids, reference should be made to the original papers. At the moment of writing no evidence incompatible with the theory has been discovered. E. A. and H. T. Graham stated that the theory would not account for the repression of swelling by sugars, but Wilson pointed out that the difference in molal fugacity of the sugar in the two phases due to the differences in ion concentrations is sufficient to account for the repressing action of sugar.

The possibilities of gain to pure science fully justify the undertaking of the enormous amount of work still to be done on the theoretical side of imbibition and the problem appears to lie as much in the field of the mathematician as in that of the chemist.

### Recent Publications on Imbibition of Gels.

(*See also* bibliography at end of Part II.)


Arisz, L. 'The Sol and Gel State of Gelatin Solutions.' I. Gelatinising. II. Swelling. 'Koll. Beihefte,' **7**, 1 (1915). Size of gelatin particles and attractions between them probably decrease during swelling. Swelling and solution are considered two stages of the same process, indefinite swelling amounting to solution.

Bennett, H. G. 'The Swelling of Gelatin.' 'J. Soc. Leather Trades Chem.', **2**, 40 (1918). Polemical.

Fischer, Martin H. Edema and Nephritis. (J. Wiley & Sons, 1915.) On Hydration and "Solution" in Gelatin. 'Science,' **42**, 223 (1915). A warning against the general adoption of the view that the "solution" of a protein represents but the extreme of that which in a lesser degree is called swelling. Hydration or swelling is to be regarded as a change through which the protein enters into physicochemical combination with water; "solution" as one which can be most easily understood as the expression of an increase in the degree of dispersion of the colloid.

Fischer, M. H. and Sykes, A. 'The influence of Non-electrolytes on the Swelling of Protein.' 'Kolloid-Z.' **14**, 215. Non-electrolytes decrease the degree of swelling of protein the more so the greater the concentration. The conclusion is drawn that the phenomenon is one of adsorption rather than osmosis.

'The Non-acid and Non-alkaline Hydration of Proteins.' 'Kolloid-Z.' **16**, 129 (1915). In the swelling of gelatin by urea, there are two changes, one towards increasing hydration, the other towards increasing degree of dispersion.

Fischer, M. H. and Hooker, M.O. 'On the Swelling of Gelatin in Polybasic Acids and their Salts.' 'J. Am. Chem. Soc.' **40**, 272 (1918).

FISCHER, M. H., and BENZINGER, M. 'On the Swelling of Fibrin in Polybasic Acids and their Salts.' 'J. Am, Chem. Soc.' **40**, 292 (1918).

FISCHER, M. H., and COFFMAN, W. D. 'On the Liquefaction or "Solution" of Gelatin in Polybasic Acids and their Salts.' 'J. Am. Chem. Soc.' **40**, 303 (1918).

GRAHAM, E. A., and GRAHAM, H. T. 'Retardation by Sugars of Diffusion of Acids in Gels.' 'J. Am. Chem. Soc.' **40**, 1900 (1918).

HATSCHEK, EMIL. 'Viscosity and Hydration of Colloidal Solutions.' 'Biochem. J.' **10**, 336 (1916).

'An Analysis of the Theory of Gels as Systems of Two Liquid Phases.' 'Chem. News,' **116**, 167 (1917).

KATZ, J. R. 'Micella are not necessary for the Explanation of Uncomplicated Swelling.' 'Z. Physiol. Chem.' **96**, 255 (1916). The facts are fully covered by the theory of a solid solution of water in the swellling substance, and in Nägelli's theory *micella* can be replaced by *molecules*.

'The Laws of Swelling. The Swelling in Water without Complications.' 'Kolloidchem. Beihefte,' **9**, 1 (1917).

LENK, EMIL. 'Importance of Electrolytes for Swelling Processes": A. The Action of the Individual Electrolytes. B. Combinations of Electrolytes.' 'Biochem. Z.' **73**, 15 and 58 (1916). The conclusion is drawn that the antagonistic actions of ions must be due to colloidal phenomena and not to osmotic pressures.

LOEB, JACQUES. 'Ionization of Proteins and Antagonistic Salt Action.' 'J. Biological Chem.' **33**, 531 (1918).

'The Stoichiometrical Character of the Action of Neutral Salts upon the Swelling of Gelatin.' *Ibid.* **34**, 77 (1918).

MANABE, K., and MATULA, J. 'Physical Changes in the States of Colloids.' XV. Electrochemical Investigations of Acid Albumin. 'Biochem. Z.' **52**, 369 (1913). The work involved the electrometric determinations of the hydrion and chloridion concentrations of hydrochloric acid solutions of serum albumen and of gelatin.

OSTWALD, WOLFGANG. 'Importance of Electrolytes for Swelling Processes.' 'Biochem. Z.' **77**, 329 (1916).

PAULI, W., and HIRSCHFELD, M. 'Alteration in the Physical Conditions of Colloids.' XVIII. Protein Salts of Different Acids. 'Biochem. Z.' **62**, 245. Equal concentrations of protein bind less of a weak than of a stronger acid.

PROCTER, H. R. 'On the Action of Dilute Acids and Salt Solutions upon Gelatin. 'Kolloidchem. Beihefte,' 1911; 'J. Am. Leather Chem. Assn.' **6**, 270 (1911. This paper contains a great deal of valuable experimental data.

'The Equilibrium of Dilute Hydrochloric Acid and Gelatin.' 'J. Chem. Soc.' **105**, 313 (1914).

'The Combination of Acids and Hide Substance.' London 'Collegium,' 1915. A paper dealing with the subject in a more popular style.

'The Swelling of Gelatin.' 'J. Soc. Leather Trades Chem.' **2**, 73 (1918). A reply to Bennett's paper of the same title.

PROCTER, H. R., and WILSON, J. A. 'The Acid-Gelatin Equilibrium.' 'J. Chem. Soc.' **109**, 307 (1916).

'The Swelling of Colloid Jellies.' 'J. Am. Leather Chem. Assn.' **11**, 399 (1916).

RINGER, W. E. 'Further Studies on Pekelharing's Pepsin.' 'Z. Physiol. Chem.' **95**, 195 (1915). The action of pepsin and swelling of protein are closely related.

'Further researches upon Pure Pepsin.' 'Proc. Akad. Wetenschappen,' **18**, 738 (1915). The point of maximum swelling of protein does not occur at the same hydrion concentration with different acids.

'The Importance of the Condition of the Substrate in the Action of Pepsin.' 'Kolloid-Z.' **19**, 253 (1916).

ROBERTSON, T. B. 'The Physical Chemistry of the Proteins.' (Longmans. Green & Co., 1918.)

ROSENBOHM, E. 'The Heat of Swelling of Colloids.' 'Kolloidchem. Beihefte,' **6**, 177 (1914). The swelling of gelatin appears to be divided into two phases, the first where a small amount of water is taken up and all the heat of swelling is evident, and the second where a large amount of water is taken up and no heat evolved.

TOLMAN, R.C., and STEARN, A.E . 'The Molecular Mechanism of Colloidal Behaviour.' I. The swelling of Fibrin in Acids. 'J. Am. Chem. Soc, **40**, 264 (1918).

WILSON, J. A. 'Retardation by Sugars of Diffusion of Acids in Gels.' 'J. Ams Chem. Soc.' **41**, 358 (1919). A reply to the statement by E. A. and H. T. Graham (*see* above) that Procter's theory cannot account for the repression of the swelling of acid-swollen gelatin by sugar.

WILSON, J. A., and WILSON, W. H. 'Colloidal Phenomena and the Adsorption Formula.' 'J. Am. Chem. Soc.' **40**, 886 (1918). A further mathematical development of Procter's theory of the swelling of colloid jellies and its relation to other branches of colloid chemistry.

WOLFF, L. K., and BÜCHNER, E. H. 'The Behaviour of Jellies towards Liquid, and their Vapours.' 'Verslag. K. Akad. Wetenschappen,' **21**, 988 (1912) and **22**, 1323 (1914). It is contended that von Schroeder's observation that the amount of water in gelatin swollen in liquid water decreases when the gelatin is placed in water vapour rests upon a defective method of experimentation.

## IMBIBITION OF GELS. PART II.—INDUSTRIAL APPLICATIONS.

*By* JOHN ARTHUR WILSON, *Chief Chemist, A. F. Gallun & Sons Co., Milwaukee.*

Imbibition plays a most important role in the manufacture of leather, paper, textiles, and many other colloidal products, but few cases are generally known of applications of theory to manufacturing conditions. In view of the fact that Procter's theory grew from an investigation of the process of pickling hides, it is not surprising that what applications of it have so far been published have been connected with the *leather industry*, especially since many of the formulas are of recent derivation. A general survey of applications, to the leather industry has been given by Procter in the First Report pp. 5–20, and need not be repeated here. Wilson and Kern used the theory to explain causes for certain discrepancies in tannin analyses made by the hide-powder method, which is widely employed both in Europe and America. One direct outcome of the theory of imbibition is the Procter–Wilson theory of vegetable tanning, which like its parent theory is largely mathematical in character. The equations forming part of the theory enable one to regulate the astringency of the tannins, their rate of diffusion into the hide, and the degree of plumping of the hide fibres, by simple alterations of the concentrations of electrolytes in the tan liquors.

Bovard, in pointing out the importance of imbibition to the *manufacture of paper*, claims that the character of the sheet is largely determined by the degree of hydration and length of the fibres. He noted that cellulose swells more rapidly in alkaline than in neutral or acid solutions, and since the rosin size used in paper manufacture is alkaline, he reasoned that the hydration of the stock would be

promoted if the size were added to the beater before the alum. In an actual test, working in this order, the paper tested 1½ points higher than that made by putting the alum into the beater first.

*Photographic* workers sometimes experience a most annoying reticulation of the surfaces of negatives, particularly when fixing or washing during hot weather. The wet gelatin layer becomes finely wrinkled or corrugated, the network of puckers forming a pattern. Sheppard and Elliott have found two causes for this difficulty. When sheets of gelatin swell or contract slowly, they undergo a change in volume but not in shape. On the other hand, the gelatine on a negative must undergo a change in shape, since one face of it is held to the plate. So long as the amount and rate of swelling are not great, no trouble is experienced, but when the swelling is excessive, due to higher temperatures or chemicals in the fixing bath, the upper surface of the gelatin will have an area so much greater than the lower surface as to cause puckering. The second cause is the presence in the solution with which the plate is treated of both swelling and contracting agents. Reticulation is readily produced by immersing the plate in a solution containing acetic and tannic acids, the former tending to swell or soften the gelatin, the latter to contract or harden it. Their rates of diffusion are determined by their effects upon the gelatin, and the result is a mosaic-like alternation of hardening and softening effects, the ridges being more swollen and the valleys contracted by tanning.

Judging from the literature available, the most extensive applications of imbibition have been in the field of *biology*. Almost without exception, this has been done by analogy, rather than by application of theory. Fischer's book, "Edema and Nephritis" is replete with analogies between inbibition of such proteins as gelatin, fibrin, and gluten, and that of things so widely different as muscles, eyes, nervous tissues, catgut, and living frogs. Loeb showed that the behaviour of dried pig's bladder in solutions of various salts very closely resembles that of powdered gelatin in the same solutions. Reference should also be made to Loeb's work on the fundulus egg, to Arnold's studies of the swelling of human muscle, and Traube's work on the swelling and germination of plant seeds.

Recent Publications Dealing with the Application, or Suggesting an Application of the Subject of Imbibition of Gels.

(*See also* Bibliography at end of Part I.)

Arnold, R. 'The Swelling Capacity of Different Kinds of Muscle in Acid Solutions.' 'Kolloidchem. Beihefte,' **5**, 511 (1914). The structure of human muscle is not a criterion of its relative swelling capacity.

Bovard, W. M. 'Colloidal Chemistry in Papermaking.' 'Paper' **22**, 11 (1918). Shows the importance of controlling hydration of the stock in making paper.

Fischer, M. H. ':Relation between Chloride Retention, Edema, and "Acidosis." 'J. Am. Med. Assn.' **64**, 325 (1915).

'The Classification and Treatment of the Nephritides.' 'The Journal-Lancet,' July 1, 1916.

Fischer, M. H., and Hooker, M. O. 'Trench Nephritis.' 'The Int. Assn. of Med. Museums,' Bulletin No. VII., May, 1918.

'Ternary Systems and the Behaviour of Protoplasm. 'Science, **48**, 143 (1918). Many of the laws governing the hydration and dehydration of soaps

are identical with those governing the hydration and dehydration of certain proteins, which in turn show analogies to living cells.

HARRISON, W. 'Investigations on the Physical and Chemical Properties of Cotton. Report of 'The Nat. Assn. of Cotton Mfrs.', 1916.

LOEB, JACQUES. 'The Mechanism of the Diffusion of Electrolytes through the Membranes of Living Cells.' I. The Necessity of a General Salt Effect upor the Membrane as a Prerequisite for this Diffusion.' 'J. Biol. Chem.' **27**, 339 (1916). II. The Diffusion of Potassium Chloride out of the Egg of the Fundulus and the Relative Efficiency of Different Ions for the Salt Effect. *Ibid.*, 353. III. The Analogy of the Mechanism of the Diffusion for Acids and Potassium Salts. *Ibid.*, 363.

'The Similarity of the Action of Salts upon the Swelling of Animal Membranes and of Powdered Colloids. *Ibid.*, **31**, 343 (1917).

PROCTER, H. R. 'Recent Developments in Leather Chemistry. 'J. Royal Soc. Arts,' 1918.

'Colloid Chemistry of Tanning. 'First Report,' p. 5.

PROCTER, H. R., and BURTON, D. 'The Swelling of Gelatinous Tissues.' J. Soc. Chem. Ind.' **35**, 404 (1916). Treats the subject from the viewpoint of the leather chemist.

PROCTER, H. R. and WILSON, J. A. Theory of Vegetable Tanning. J. Chem. Soc.' **109**, 1327 (1916).

SHEPPARD, S. E., and ELLIOTT, F. A. 'The Reticulation of Gelatin.' J. Ind. and Eng. Chem.' **10**, 727 (1918). An application to photography.

TRAUBE, I., and KÖHLER, F. 'The Velocity of Formation and Solution and of Swelling of Gels.' 'Intern. Z. Biol.' **2**, 42 (1915). A discussion is given of the relation between experimental results and the following biological problems: narcosis, plasmolysis of cells, chemotaxis, muscular work, edema, and inflammations.

TRAUBE, I., and MARUSAWA, T. 'Swelling and Germination of Plant Seeds.' 'Intern. Z. Physik. Chem. Biol.' **2**, 370 (1915).

UPSON, F. W., and CALVIN, J. W. On the Colloidal Swelling of Wheat Gluten.' 'J. Am. Chem. Soc.' **37**, 1295 (1915).

WILSON, J. A. 'Theories of Leather Chemistry.' 'J. Am. Leather Chem. Assn.' **12**, 108 (1917).

'Theory of Tanning,' *ibid.*, **13**, 177 (1918).

'Theory and Practice of Leather Chemistry,' *ibid.*, **14**, 93 (1919).

WILSON, J. A., and KERN, E. J. 'The Non-Tannin Enigma.' 'J. Am. Leather Chem. Assn.' **13**, 429 (1918).

## COLLOID PROBLEMS IN BREAD-MAKING.

*By* R. WHYMPER, *Chief Chemist to Messrs. Peek, Frean & Co., Ltd., Biscuit Manufacturers, London, and late Assistant Inspector of Bakeries, B.E.F., France.*

There is no manufacturer less aware of the chemical problems underlying his trade than the master baker. In spite of his ignorance, however, he is one of the most efficient members of society, in that he produces an excellent article with great regularity. This is, perhaps, less a matter of wonder when it is realised that the art of bread-making of a high order can be traced through the Chinese to about 2,000 years B.C., and is of course older than that, and that even to this day the majority of people can make a very passable loaf.

Such scientific work as has been done, in or for the bakery, has usually been undertaken for some specific material object, for advantage to the large manufacturer (yields, moisture retainers, effect of machinery) or for the protection of the consumer (sanitary conditions of manufacture, effect of alum, bleaching agents, &c.). There is comparatively

little published work available to show that the problems have been tackled for a scientific purpose, or for improvement of the process. Indeed, there has been no stimulus for the chemist, since, in the bakery the ability of a master baker to feel, taste and smell the ingredients is a more sure guide in the production of good bread than the knowledge obtained by use of test tubes and balance.

It will be observed that the two points of view, that of the producer and that of the consumer, are largely but not entirely sympathetic. The former, whether the small hand-baker or large manufacturer, demands the greatest yield from his ingredients, and the most attractive-looking product, but really is not greatly concerned about the flavour, provided he can sell his bread. The result is the exhibition loaf of perfect proportion, if somewhat insipid, or the water-laden and profitable loaf, both the outcome of scientific treatment. All the consumer asks to-day is that his bread shall be palatable, and be made in a cleanly manner and cheap, whilst he is not greatly interested in the amount of water present in his loaf. Such a loaf, to suit the consumer, can generally be assured by the hand-baker. It is therefore rather in the economic direction that any considerable amount of work has been done by the bakery chemist, who himself is only just beginning to realise the variety and complexity of the problems underlying the art. That he will, at a near date, assume supreme importance in the bakery, especially in the large machine or automatic bakery, is certain, but the time is not yet, for he does not know enough and, above all, the master baker is well aware of the fact. It is easy to analyse all the ingredients in use in the bakery, but it is less easy to determine how a combination of these ingredients will turn out as bread, since the mutual influence of one complex upon another is not known with any degree of certainty.

It is unfortunate also that so many technologists, having acquired a smattering of chemistry, pose as scientific experts, with the result that conflicting opinions, arising from the interpretation of inaccurate results, have injured the prestige of the chemist. On the other hand, the chemists have not been free from the fault of supplying, from a laboratory, advice which clearly indicates that they do not know the elements of bread-making.

Briefly put (for it must be assumed that the elementary principles of bread making are understood by the reader), bread is made from flour, yeast, water and salt, with occasionally milk, fat, malt extract, yeast salts, wheat germ, aerating chemicals, &c., according to the quality of bread required, English bread, farmhouse bread, milk bread, germ bread, malt bread, tin loaves, Viennese rolls, French rolls, &c.

With the addition of any new ingredient over the first four mentioned, fresh complications in the chemical changes during bread-making are introduced. Added to these must be considered the changes involved during fermentation and baking, and, one of the largest problems of all, during the change from freshness to staleness which the loaf undergoes with the passage of time. With the use of flour, yeast, water and salt alone, a mixing of dough, and the subsequent loaf, are of sufficient complexity, involving the saturation

and swelling of the starch granules (for future gelatinisation by heat), the production of hydrated forms of gluten, itself a complex proteid, biological changes during the growth of yeast, the occlusion of gas evolved during that growth, the action of the yeast enzymes on the carbo-hydrates, the working of the dough to secure suitable elasticity, proteolytic enzyme action on the gluten, the hardening action of salt on the gluten, gelatinisation and saturation of the starch-water system on baking, and the gradual changes, physical and chemical, during cooling and ageing which bring about eventual staleness. This is but a broad outline of the problems to be attacked when the barest necessities for the production of bread are used, and it is evident that the addition of milk or fat must increase the complication of the bread system.

## I.—*Flour.*

The flour components of greatest importance are starch, gluten, mineral salts and enzymes.

### (a) *Starch.*

Some space has already been devoted in Report I. (p. 46 *et seq.*) to the consideration of wheat starch and its behaviour in the presence of water at a temperature to cause gelatinisation. It is not intended to cover this ground again.

Wheat starch in the presence of a sufficiency of water will commence gelatinisation about 60° C., and every granule will be completely burst at about 65° C. Since the baking temperature of a bread oven is usually between 200° and 240° C., and the amount of water present in a normal dough is about 41 per cent., the baking lasting for one hour, it might be imagined that, all other factors removed, a great proportion of the starch granules to be found in bread-crumb would be gelatinised. Yet, as a rule, the starch granules inside a loaf show a mixture of those untouched by the damp heat and of those only slightly swollen, whilst a few only have undergone complete gelatinisation. The reason for this divergence from theory may be found in the fact that a temperature seldom higher than 95° C. is reached within the loaf, and then only for a very short period, during the baking hour, though temperatures as high as 99·5° C. have been recorded. It is probable that the time factor is of some importance here. Further, the saturation of starch by water is reached when a mixture shows 41 per cent. of the latter, hence, after allowing for the absorption of water by gluten (which is not inconsiderable, being as much as 200 per cent. of the dry gluten of a strong flour and slightly less for weaker flour), there is an insufficiency of water present to allow complete gelatinisation of all the starch granules at the temperature of baking. The complexity of the colloid systems in a baked loaf is, therefore, considerable.

Were there no component other than starch to consider, such problems as the change in physical consistency from freshness to staleness of a loaf would be comparatively easy of solution. But there are so many underlying difficulties connected with dissolution by enzymic action on the one hand, and coagulation by electrolytes on the other, that the behaviour of the colloids in the loaf after

baking is less easy to interpret. It must not be forgotten, moreover, that gluten, so far as can be ascertained, hinders the deposition of starch from its jelly. At any rate, by the addition of extra gluten to flour-dough the resulting bread possesses better keeping qualities, which, from our recent researches (Whymper, R., "*The Conditions that Govern Staleness in Bread*," *Maclaren and Sons, Ltd.*, 1919) in the Army, have been shown to depend chiefly upon the rate of deposition of starch from its solutions with the passage of time. In other words, gluten acts as a protective colloid to starch in solution. Exception may be taken to such a generalisation as this, on the ground that it is the quality of the gluten that determines whether bread will keep well or quickly become stale. Snyder (*U.S. Dept. Agric., Bull.*, 101, 56, 1901) found that the addition of starch or the addition of gluten, the former up to 20 per cent. of the flour, was without material effect upon the size of the loaf, though the water-absorbing capacity of the starchy flour was reduced. We are of the opinion, however, that the conclusion reached by that worker and by Jago ("*The Technology of Bread-Making*," 1911, p. 305), that "the character rather than the quantity of the gluten content" governs the quality of bread, is too far-reaching, since they omitted to consider the keeping qualities of the loaf. Jago's figures for the viscometer readings of a similar experiment are not without interest (Table I.), for, though of a rough order, they give some indication of a previously observed fact, that, in the case of flours of high water-absorbing capacity, this power is retained but little diminished on being reduced to a uniform wet gluten-percentage level by the addition of wheat starch.

TABLE I.

*Viscometer Determinations on Mixtures of Flour and Starch.* (Jago.)

| | I. Spring American Patent. | II. Winter American Patent. | III. Second Class Winter American Bakers. | IV. Hungarian Patent. | V. English Wheat Patent. | VI. British Milled First Patent. | VII. British Milled Second Patent. |
|---|---|---|---|---|---|---|---|
| Original percentage of wet gluten - | 39.2 | 28.2 | 32.0 | 35.0 | 27.75 | 31.9 | 38.4 |
| Water-absorbing power by viscometer - - | 68.6 | 54.8 | 69.0 | 76.0 | 61.0 | 60.5 | 64.0 |
| Viscometer readings on gluten being reduced by admixture of starch to— | | | | | | | |
| 35 per cent. - | 65.0 | — | — | — | — | — | — |
| 30 ,, - | 62.7 | — | — | 71.3 | — | 60.0 | 63.0 |
| 25 ,, - | 62.0 | 55.5 | 66.0 | 70.7 | 59.5 | — | — |
| 20 ,, - | 61.4 | 55.4 | 62.0 | 66.0 | 57.5 | 57.5 | 58.5 |
| Weight of starch added to 100 parts of flour to reduce gluten to 20 per cent. - - | 96.0 | 41.0 | 60.0 | 75.0 | 38.75 | 59.5 | 92.0 |

With regard to starch solutions and starch pastes, some viscosities have already been given. (Report I., p. 47. *See* especially Samec, 1911, *Koll. Chem. Beihefte*, **3**, 123–160; 1912, *idem*, **4**, 132–174; 1913, *idem*, **5**, 141–210.) Elsewhere ("*The Conditions that Govern Staleness in Bread*," 1919) the present writer has observed that "the change in viscosity, with time, of starch paste follows a general rule in that, at first thinly viscous when first prepared (hot), it sets to a jelly, and later becomes thinly viscous again." Pure supsensoids change their viscosities (usually a decrease) in days, the more typical emulsoids showing an increase in viscosity much more quickly. It is assumed that, in starch paste, the latter changes are masked by the slower changes of the former. As a matter of fact, the curve (viscosity plotted against time) is of a distinct S shape, the changes being more marked the more concentrated the solution. The solutions worked with were prepared by digesting 8 grams of wheat starch (containing 10·8 per cent. water) in 180 c.cs. of water, and boiling till the clearest paste was obtained. Other figures of interest obtained with such a solution are shown in Table II., but should be compared with those in Table III. showing the same methods applied to Doughs and Bread-crumb, since, in every case, it is clear that the principle underlying changes in starch paste need not necessarily be reproduced in bread-crumb, in which the phases are so differently distributed.

TABLE II.

*Starch Paste.*

| — | —— | Apparent Moisture, per cent. | Soluble Extract* on Bone-dry Solids per cent. | Colorimetric Value of Extract with standard Iodine solution. |
|---|---|---|---|---|
| I | After 30 minutes cooling | 95·90 | [19·15] | 1·31 blue |
| II | „ 6 hours „ | 95·95 | [12·74] | 1·05 „ |
| III | „ 24 „ „ | 95·92 | [7·62] | 0·12 „ |
| IV | „ 48 „ „ | 95·97 | [19·5] | 0·07 „<br>0·04 red |
| V | „ 72 „ „ | 96·84 | [16·55] | 0·04 blue<br>0·05 red |
| VI | „ 96 „ „ | 95·95 | [17·26] | 0·08 blue<br>0·21 red |
| VII | „ 144 „ „ | 95·99 | [33·91]† | 0·34 blue<br>0·20 red |

* These values are unreliable, owing to magnification of experimental error by calculation.

† After 150 hours a still higher figure was obtained.

TABLE III.

*Doughs and Bread-Crumb.*

| —— | Loaf weights in grams. | Apparent Moisture per cent. | Soluble Extract on Bone-dry Solids per cent. | Colorimetric Value of Extract with standard Iodine solution. |
|---|---|---|---|---|
| Dough after mixing | — | 41·21 | 10·07 | 0·21 red<br>0·05 yellow |
| Dough after proving | — | 41·10 | 9·76 | Nil. |
| Bread 6 hours old | Original 997<br>6 hours 973 | 41·42 | 12·84 | 1·10 blue<br>2·50 red |
| Bread 70 hours old | Original 995<br>6 hours 972<br>24 hours 964<br>48 hours 952<br>70 hours 945 | 41·35 | 15·31 | 0·15 blue<br>0·25 red |

Among other conclusions reached by this research were :—

1. The loss of water during cooling and drying-out of a loaf is not responsible for staleness.

2. During the process of becoming stale, there is a fall in soluble extract obtained from the crumb, followed, after a time, apparently independent of staleness, by a rise. The soluble starch in bread-crumb (as shown by the iodine colouration) drops rapidly between 6 hours' and 24 hours' cooling.

3. Investigation shows that a similar fall and rise of soluble extract is to be seen in starch pastes, whilst the iodine colouration follows the same rule observed in bread-crumb.

4. Staleness may be attributed to—

(i) Deposition of solid starch in the crumb of bread, starting between 6 hours and 24 hours' cooling period—

(*a*) By change of temperature;

(*b*) Accelerated by the presence of solid starch particles already existing in the crumb.

(ii) Partial polymerisation of starch, independent of the deposition already stated, which tends to crumble the gelatinous nature of the bread-crumb when fresh.

The statement in 4 (i) (*b*) is open to dispute, for we have no actual proof that the deposition of solid starch from solution is accelerated by the presence of other solid particles. This work is even now in progress. On the other hand, the statement made in para. 4 (ii) is, we believe, substantially correct, for the following reasons, which must be taken in conjunction with the figures given in Table II showing the soluble extracts from starch paste decreasing with time, (especially as indicated by the iodine colouration) :—

If we take the suspension of starch granules in water as the starting point of our consideration, it is seen to be a coarsely disperse system,

or a crude suspension of colloid matter in a dispersion medium, increasing in uniformity of distribution as the subdivision of the suspended particles is increased. Such a system allows almost complete separation of the dispersion means by filtration through an ordinary filter paper. The ordinary filter paper will hold back particles having a diameter greater than about 5$\mu$, though, according to the method of preparation, filters can be obtained which will stop the passage of particles down to an approximate diameter of 2 $\mu$. According to E. F. Armstrong (Brit. Assocn., 1909), the smallest wheat starch granules vary from 3 to 5 $\mu$, and the largest from 30 to 35 $\mu$, so that the filtration of the water from the granules should be almost complete. This, in practice, has been observed to be the case.

The simplest form of starch has been given (Brown, H. T., and Morris, G. H., *Jour. Chem. Soc.*, **53,** 610, 1888) a molecular formula $[(C_{12}H_{20}0_{10})_{20}]_5$. Lobry de Bruyn and Wolff (*Rec. Trav. Chim. des Pays. Bas.*, **23,** 155, 1904) estimated the size of the starch molecule to be approximately 5 $\mu\mu$, as compared with hydrogen gas 0·067–0·159 $\mu\mu$, and water vapour 0·113 $\mu\mu$. Soluble starch prepared by the action of ozone on common starch was examined by Friedenthal (*Physiol. Zentralbl.*, **12,** 849, 1899). who obtained a molecular weight of 9,450 as against 32,400 in the formula above. The product obtained in this way was clearly more highly dispersed than ordinary starch, a fact borne out by the definite depression of the freezing point of water containing it in contrast to a suspension of ordinary starch or to a starch paste.

*Depression of Freezing Point of Soluble Starch.*

| Concentration per cent. | Depression of the Freezing Point. |
|---|---|
| 2·5 | 0·005 |
| 5·0 | 0·01 |
| 10·0 | 0·02 |

On the figures of Lobry de Bruyn and Wolff, " if a cubic centimeter of dry starch could be subdivided into its molecules or dissolved in the ordinary sense of the word, the starch would present a total surface of several thousand square metres towards the solvent," and, in doing so, would pass from an average size of its individual particles of 20 $\mu$ through the value 0·1 $\mu$, which represents the limit of microscopic visibility, to a value of 1 $\mu\mu$, a figure somewhat smaller than that of a particle hitherto observed with an ultra-microscope.

It is between the last two values that colloid chemistry has to deal, according to Zsigmondy's system of classification. (Zsigmondy, R., *Zur Erkenntnis der Kolloide*, XXII., Jena, 1905.)

With regard to filtration of colloids through various papers and diaphragms, a considerable amount of work has been done, the most interesting for the immediate purpose being that by Bechold (*Zeitsch. physik. Chem.*, **64,** 328, 1908). Bechold's results, from his experiments with the pores of filter papers, cannot be taken as absolutely accurate during prolonged filtration of colloid solutions,

since absorption effects are often observed, due to the action of the paper on the dispersed phase, and often lead to clogging of the pores of the filter. The results are, however, interesting, since they show that typical colloids, with particles having a diameter less than 0·1 $\mu$, are easily able to pass through all the filters tested.

*Size of Pores in Filters.*

| Filter. | Average Size of Pores (Permeability to Water). |
|---|---|
| Ordinary thick filter paper - - - | 3·3 $\mu$ |
| Filter paper, No. 556. (Schleicher and Schüll) - - - - - - - | 1·7 $\mu$ |
| Filter paper, No. 602. (Extra hard, Schleicher and Schüll) - - - - | 0·89–1·3 $\mu$ |

The degree of solubility is also of importance in this question of filtration, chiefly because the solubility of a substance is dependent upon its specific surface, or, in other words, the solubility rises greatly with the extreme subdivision. The jelly concentration of silicic acid was found by Graham (*Jour. Chem. Soc.*, 1864), in the very early days of colloid chemistry, to influence the maximum molecular solubility in excess of water. Thus he found that only two parts of 1 per cent. silicic acid jelly formed a molecular disperse solution in 10,000 parts of water, one part of a 5 per cent. jelly, and less of greater concentrations of jelly in the same amount of water. Concentrated jellies, therefore, are less disperse than the more dilute, and so have a lower molecular solubility. The low solubility of gelatinised starch will be appreciated when the figures shown in Tables II. and III. are compared.

The viscosity of starch solutions and separation of starch paste into two phases has already been pointed out in the First Report (p. 49), but, before passing to other points, it is as well to consider another aspect of true soluble starch. Some description of soluble starch has already been given in a previous Report (No. I., p. 51), but there is little doubt that confusion has arisen owing to its variable nature according to the method of its preparation.

*Soluble Starch.*—Soluble starch paper, prepared by the action of diastase or acids on starch paste or by heating dry starch in a suitable manner (Zalkowski, *Chem. Zeit.*, 1888, 1060), is soluble only to a very small extent—about 2·3 per cent.—in cold water, yet it is possible to obtain a preparation, by the action of sodium peroxide (Syniewski, *Ber.*, 1897, XXX., 2415) on starch suspended in water, that is soluble to the extent of some 12 per cent. in the cold. The latter seems quite a different compound to that prepared by Lintner's method with diastase.

The varied descriptions of the behaviour of soluble starch when placed in water, dissolved and subsequently cooled, would add weight to the conclusion that it was not always the same kind of soluble starch that was under consideration. It may, and usually does, form a thin opalescent paste, remaining fluid on cooling, however prepared, but it does not always revert to the insoluble form in time. Fouard (*Compt. Rend.*, 1908, **97,** 931–3) used a soluble starch that reverted

apparently in a comparatively short time, whilst the writer, in Table IV., has shown that, if there were any reversion at all after 144 hours, in the soluble starch that he employed, it was quite insignificant. There is undoubtedly a small quantity of true soluble starch formed in bread-making.

TABLE IV.

*Soluble Starch.* (From Messrs. Baird and Tatlock.)

| — | —— | Apparent Moisture per cent. | Soluble Extract* on Bone-dry Solids per cent. | Colorimetric Value. |
|---|---|---|---|---|
| I | After 30 minutes' cooling | 95·97 | [82·38] | 1·78 blue |
| II | ,, 6 hours' ,, | 96·05 | [84·05] | 1·00 ,, |
| III | ,, 24 ,, ,, | 95·93 | [77·64] | 1·68 ,, |
| IV | ,, 48 ,, ,, | 96·04 | [77·52] | 1·95 ,, |
| V | ,, 72 ,, ,, | 95·94 | [72·66] | 1·90 ,, |
| VI | ,, 96 ,, ,, | 96·06 | [89·34] | 1·43 ,, |
| VII | ,, 144 ,, ,, | 96·69 | [83·38] | 1·33 ,, |

* These figures are open to less error than those for starch paste, owing to the greater amount of soluble matter actually present.

(b) *Gluten.*

Wheat gluten has been briefly referred to in Report I. (p. 72), from which it may be gathered that the proteid is itself a mixture of coagulable albumin, glutin, and gliadin. These more or less distinguishable proteids have been again subdivided by Osborne and Voorhees (*Amer. Chem. Jour.*, 1893, "*The Proteids of the Wheat Kernel*") into glutenin, gliadin, globulin, albumin, coagulum, proteose, and certain nitrogen compounds soluble inwater in the following proportions, for flour milled from specified wheat :—

TABLE V.

*Composition of Wheat Gluten.* (Osborne and Voorhees.)

| | Spring Wheat. | | | Winter Wheat. | | |
|---|---|---|---|---|---|---|
| — | Nitrogen × 5·68 | = | Proteid. | Nitrogen × 5·68 | = | Proteid. |
| Glutenin - - | 0·8245 | = | 4·683 | 0·7346 | = | 4·173 |
| Gliadin - - | 0·6977 | = | 3·963 | 0·6884 | = | 3·910 |
| Globulin - - | 0·1148 | = | 0·624 | 0·1148 | = | 0·625 |
| Albumin - - | 0·0657 | = | 0·391 | 0·0603 | = | 0·359 |
| Coagulum - - | 0·0453 | = | 0·269 | 0·0379 | = | 0·223 |
| Proteose - - | 0·0341 | = | 0·213 | 0·0791 | = | 0·432 |
| From water-washings of Gluten. | 0·2239 | = | 1·272 | 0·1552 | = | 0·881 |
| Total - | 2·0050 | = | 11·415 | 1·8703 | = | 10·603 |
| In meal - - | 2·10 | = | 11·93 | 1·94 | = | 10·96 |

Gluten of wheat flour is therefore a variable colloid when met with in the bakery. It is upon the proportion of glutenin to gliadin and upon the amount and quality of salts present that the nature of the gluten of wheat flour depends. Unless these proportions are known (obtainable only by laborious effort in the laboratory), it is not possible for the chemist to predetermine the quality of the resulting bread. "Washing out" accompanied by baking trials are the speedier tests for the quality of a flour.

Glutenin is insoluble in water, saline solutions and dilute alcohol, soluble in dilute acids and alkalis, and reprecipitated from such solutions by neutralisation.

Gliadin is insoluble in absolute alcohol; soluble in dilute alcohol, (slightly in 90 per cent. and very soluble in 70–80 per cent. alcohol), from which it is precipitated by adding a large quantity of water or strong alcohol, especially in the presence of much salts. It is soluble in distilled water, forming an opalescent solution from which it is precipitated by addition of sodium chloride.

Globulin is soluble in sodium chloride solutions, precipitated therefrom by dilution or saturation with magnesium sulphate or ammonium sulphate, but not with sodium chloride. Partly precipitated by boiling, but not coagulated at temperatures below 100° C.

Albumin is precipitated from its solution by saturating with sodium chloride or magnesium sulphate. Coagulated at 52° C.

Coagulum and proteose are both probably formed during the extraction of the gluten with water. The former is precipitated by saturating its solution with sodium chloride, or by adding 20 per cent. of sodium chloride and acidulating with acetic acid. On concentrating this solution, the proteose is coagulated, leaving behind a proteid called coagulum, which has not been separated in a pure state.

The behaviour of wheat gluten under the influence of salts is, therefore, clearly the result of complex and mutual action among the various colloid components and electrolytes. Very little more can be said definitely.

Ostwald and Lüers [*Koll-Zeits.* **25,** 26–45, 82–90, 116–136, 177–196, 230–240 (1919); **26,** 66–67, (1920)] were evidently working on the colloid chemistry of bread at the same time as the present writer who, unfortunately, has not had an opportunity of seeing the complete papers. The general results obtained seem, however, to bear out the conclusions reached by us in 1918, and published in the *British Baker* in the following year. Ostwald and Lüers have found that the chief differences between flour, dough, and new and stale breads, are of a physical rather than of a chemical nature, and these workers have studied each material separately as a colloid, in much the same way as we have done. The viscosity of various mixtures of flour and water, containing as much as 20 per cent of flour, were made, and mixtures of wheat flour and water were compared against rye mixtures. It was found that rye mixtures became more viscous, whilst wheat mixtures became thinner, on standing, and that traces of acids greatly increased the viscosity of the wheat mixtures, whilst sodium chloride appeared to reduce it. One point of great importance was established, viz., that a flour of

poor baking quality invariably gave viscosity figures considerably below those of good flours.

The action of gliadin in gluten was also studied, and the viscosity of gliadin solutions was found to be increased by traces of acids and alkalis, and diminished by neutral salts. Further, the viscosity of gliadin solutions was greatly affected by change of temperature, and it is interesting to observe that the temperature at which the maximum viscosity was reached was also the temperature at which the best doughs and breads are produced.

The more recent work of Wood, on the action of acids and salts on gluten, has already been briefly outlined in the First Report, but his subsequent comments (Wood and Hardy, *Proc. Roy. Soc.*, 1909, B. 81, 38), made to bring the phenomena of the solubility of gluten into harmony with the ionisation theory, cause rather a strain upon the imagination. We may well believe that "the variations in coherence, elasticity and water content, observed in gluten extracted from different flours, are due rather to varying concentrations of acid and soluble salts in the natural surroundings of the gluten than to any intrinsic differences in the composition of the glutens themselves," but it is less easy to understand that the formation of aqueous solutions of gluten "is due to the development of electric charges round the particles of the proteid owing to chemical interaction between proteid, acid, or alkali, and water," and that the converse, "the tenacity, ductility and water-content of a solid mass of moist gluten depends upon the total or partial disappearance of these electric double layers (supposed to surround each particle of solute), and the reappearance of what is otherwise obscured by them, namely, the adhesion, or 'idio attraction' as Graham called it, of the colloid particles for each other, which makes them cohere when they come together." This may be the explanation, but it does not help us largely in predetermining the quality of the bread from any particular flour, especially as the glutens were treated after washing out and not in their normal surroundings.

Weyl and Bischoff (Jago, "*The Technology of Bread-making*") showed that a flour moistened with a 15 per cent. sodium chloride solution gave a dough that had lost its tenacity. Flour baked for several hours at 60° C. can also not be doughed. Both experiments have given rise to the theory that a ferment "myosin" is largely responsible for the ultimate production of gluten during doughing.

Distilled water dissolves a certain amount of gluten from flour, and leaves the dough sticky rather than springy. Soft alkaline water destroys the springiness of gluten by disintegration of the gluten, and by prevention of the coherence of its particles. Hard waters, especially those containing much sulphates, harden the gluten considerably. Chlorides generally are more gentle in their action and, up to a point, assist the water-absorbing and retaining power of gluten.

For other information concerning gluten and its components, see also :—

*Jour. Amer. Chem. Soc.*, 263, Guess (1900); 1068, Snyder, and 1657, Chamberlain (1905); 8, Norton (1906); 74, Matthewson (1908); 1295, Upson & Calvin (1915).

*Jour. Soc.Chem. Ind.*, 1417 Arpin (abs.) (1902); 368, Baker & Hulton (1908).
*Canadian Dept. Agric.*, [57], 37, Shutt (1907).
*Jour. Board Agric. Supp.* 4, 29, Saunders (1910); 52, Hardy (1910).
*Agric. Gaz., N.S. Wales*, Guthrie (1896).
*Compt. Rend.*, **123,** 755, Fleurent (1896); **132,** 1421, Fleurent (1901).
*Agric. Expt. Stn., Arkansas*, Bull 53, Teller (1898).
*U.S. Dept. Agric.*, Bull 101, 56, Snyder (1901).
*Zeit. anal. Chem.*, **44,** 516, Osborne & Harris (1903).
*Jour. Agric. Soc.*, **2,** 1, Humphries & Biffen (1907).

(c) *Mineral Salts.*

The character of bread and, incidentally, the character of gluten are so intimately connected with the action of mineral salts (or other electrolytes) upon colloids, that reference should first be made to the collection of information to be found in the two previous Reports. The works of Wood and Hardy have already been referred to, and scattered through the literature on colloids may be found many other references to the influence of various salts upon wheat gluten, the chemical composition and original nature of which is seldom specified.

The " maturing of gluten " is often mentioned in technical works, and means little else than modifying a " short " gluten to a condition by which it is capable of retaining the gas generated by the yeast. Kohman and Hoffman (*Jour. Ind. Eng. Chem.*, 1916, **8,** 781–9; 1917, **9,** 148–59) have made special claims for potassium bromate in this connection, and have employed it in a special yeast food which was used in the U.S.A. Army with great success. It should be noticed that the action of potassium bromate is more effective the higher the grade of flour used, both in modifying the gluten and in improving the colour and texture of the bread (*Rep. Conn. Agric. Expt. Stn., Bull*, 200, 1917). The addition of alum was but another attempt to modify a bad gluten, the hardening or coagulating effect of that chemical upon many colloids being well known (Odling, *Jour. Soc. Arts*, 1858). As a rule, alum was only employed on old or damp flour, in which the gluten had deteriorated due to the action of acetic or lactic acids. [*See also* the ancient use of sulphate of copper for improving flour. (Liebig, " *Letters on Chemistry* ").]

Deterioration with age of the physical qualities of gluten for bread-making is also well known (Whymper, R., " *Knowledge*," **36,** 85, 1913), whilst the maturing effect on flour gluten of time and bleaching materials should be considered. (*Rep. Local Govt. Board*, 1911, I. *and* II., *N.S.* 49, *Food Report* 12, by Hamill and Monier-Williams respectively.)

The nature of the water used in bread-making is of as much importance in securing quality as in brewing. It is, of course, the quality of the contained mineral salts in the water that determines the suitability or otherwise of any given source. The action of the salts is not only upon the starch and gluten colloid systems but also upon the degree and speed of development of yeast cells. The effect of soft and hard waters upon gluten has already been mentioned; that upon yeast nd fermentation can be found in any text-book (Reynolds Green, " *The Soluble Ferments and Fermentation*," &c.). It is not without interest in the latter connection that Müller

(*Ber. d. deut. chem. Gesell.*, **8**, 679, 1875) has found that diastase in the presence of $CO_2$ can act upon unboiled starch.

(d) *Enzymes.*

The colloid problems of enzymes have been reviewed in Report II., and but little can be added to this information so far as bread-making is concerned. Those enzymes that have to be considered are principally maltase, diastase, invertase, zymase, and certain proteolytic enzymes that are not easy to identify.

Of considerable interest to us is the future development of the work of Panzer (*Zeitsch. physiol. Chem.*, **93**, 316, 339, 1914) on the activation of carbohydrates. This worker found that dry lactose treated with dry hydrogen chloride and subsequently with ammonia acquires feeble amylolytic power. The same, he states, to be true of starches, dextrins, gum arabic, maltose, dextrose, lævulose, and galactose. (See also *Jour. Soc. Chem. Ind.*, 1908, 389, Ford and Guthrie.)

II.—*Yeast.*

The work of Professor Bayliss in Report II. (p. 117), surveying the existing knowledge of protoplasm, its nature and properties, and of enzymes that regulate the chemical reaction of the living organism, fully covers the experience of the bakery chemist so far as yeast is concerned. The problems are by no means simple, and involve the biological history of Saccharomyces cerevisiæ (*see* Lafar, "*Technical Mycology*") in a variety of media (*see* Jago, "*The Technology of Bread-making*," *Chap.* XI.), and the action of the enzymes contained in and produced by the yeast, as well as certain bacteria, such as the lactic, butyric, and acetic ferments. The auto-digestion of yeast is particularly interesting and important to the baker, who to-day uses, so largely, compressed yeast containing 70–75 per cent. of water In the Army in France the deterioration of yeast during the hot weather was studied, recourse to barms being frequent there in the summer months. Barms were in constant use in Gallipoli and Mesopotamia during the war.

The growth of "rope" (B mesentericus) and moulds should also be mentioned, since their presence must indicate that the bread had become a suitable medium for their propagation from internal changes, and by reason of suitable environmental conditions.

III. and IV.—*Water and Salt.*

As already indicated, the nature of the water is important in considering the quality of bread produced, and the action of various salts commonly found in water, and of sodium chloride in particular, upon the strength or quality of wheat gluten has already been outlined.

V. *et seq.*—*Fat, Milk, &c.*

The colloid nature of these ingredients has also been considered in previous reports. When used in conjunction with flour, water,

salt and yeast, in quite small quantities, their influence, both on the physical nature and on the keeping qualities of the bread (so far as staleness is concerned), is out of all apparent proportion, however, to the amount present. The present writer has already remarked elsewhere that :—

" The effect of freshness can be enormously increased and sustained for many days by the addition of small quantities of fat. With added fats, up to 3 lbs. to the sack of flour, to doughs made by the short, straight process, the colour is but little impaired, whereas the crust is shorter, the crumb sweeter and more palatable, and the effect of staleness is not appreciated for a much longer time than is the case with bread from the simple standard mixing. The use of half milk and half water, instead of all water, as liquor has a somewhat similar effect, and the bread produced from this mixing recalls the home-made farm loaf, which does not appear to change from the original state of freshness for a week or more, if kept in a cool, dry place."

The reason is not so far to seek, yet, up to the present, no figures have been obtained to demonstrate the protective influence of the colloid existence of these added ingredients upon starch solutions. There is little doubt, however, that they prevent the deposition of starch in much the same way as they oppose the setting of cements.

## COLLOID CHEMISTRY IN PHOTOGRAPHY.

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### *Introduction.*

Most photographic processes fall into one of the two following classes :—

(1) The substance sensitive to the light is eventually turned into the pigment.

(2) The substance sensitive to light is the support of a pigment already present.

In both classes of process the support of the sensitive substance or pigment is usually a dried gel, *e.g.*, collodion, gelatin, gum.

As an example of class (1) we will consider the ordinary commercial dry plate. The sensitive film consists of very small crystals of silver bromide, sometimes containing some iodide, supported in a dried gelatin gel. On exposure to light some of the grains become developable. On development—treating with a reducing agent, *e.g.*, alkaline hydroquinone—the gelatin swells and the developer diffuses into the gelatin, reaches the grains of silver bromide and reduces to metallic silver those previously made developable by light.

As an example of class 2 we will consider the carbon process. A gelatin solution containing a pigment such as finely divided carbon is coated on to a suitable support, dried, sensitised by immersion in a solution of ammonium bichromate and dried again. The print

is exposed behind a negative and is then developed by washing in warm water. Where the bichromated gelatin film has been exposed to light it has become insoluble, where it has not been exposed to light it dissolves in warm water and the pigment is washed away. Since the bottom of the film will have been protected from light by the pigment it will dissolve in water and all the gelatin film will come away from its support. It is therefore necessary to transfer the gelatin layer on to another support and to develop the image by washing away the pigment that was the bottom of the film.

### *Photographic Emulsions.*

If, to a solution of potassium bromide we add an equivalent amount of a solution of silver nitrate, we obtain a precipitate of silver bromide which quickly collects in the form of large flocks and settles to the bottom of the vessel. If the precipitate in this state or after washing, is shaken up with a solution of gelatin containing a trace of potassium bromide, a colloidal solution of silver bromide is obtained[5]. Such solutions are usually termed emulsions, though, strictly speaking, this is a misnomer they are suspensions, in which gelatin acts as a protective colloid. If the silver bromide is allowed to stand for two or three days before treatment with the gelatin and bromide, it will not form the emulsion. The usual method of preparing emulsions is to precipitate the silver bromide in the presence of gelatin. The particles in the emulsion as soon as they are prepared, are very fine indeed, and such emulsions are sometimes called grainless. If the emulsion is washed free from dissolved salts at any time and kept at ordinary temperatures it becomes fairly stable, that is to say it changes fairly slowly or not at all. If there are dissolved salts present, which have a slight solvent action on the silver bromide, an increase in the size of grain takes place. The change is favoured by rise of temperature. The grains become more sensitive to light as they grow. This growing of the grains is called "ripening." Under suitable conditions the grains grow by capilliary forces until they are $2\mu$ to $10\mu$ diameter[13]. The smaller grains being more soluble than the larger, dissolve and make the solution supersaturated with respect to the larger ones which therefore grow. Usually crystals will only grow in this way until their diameter is about $2\mu$, because above this size the solubility no longer diminishes as the size increases. The crystals of silver bromide can certainly grow to $10\mu$ diameter during ripening, and this may be due to the fact that such crystals are in the form of very thin plates (less than $1\mu$ thick), or it may be caused by unequal heating and the presence of convection currents in the solution during ripening.

The chloride and bromide of silver crystallise in the cubic systems at all temperatures used in the preparation of photographic emulsions. The iodide crystallises in the hexagonal system below 146° C., and above that temperature in the cubic system. The three halides form solid solutions with each other, so that in an emulsion containing more than one halide, we have only one kind of mixed crystals present. Although in many plates several per cent. of silver iodide is present

with the silver bromide we only get crystals of the cubic system. A microscopic examination of ripened emulsion shows that the particles vary in size from $0{\cdot}4\mu$ to about $10\mu$, but emulsions used in practice do not often contain crystals larger than from $2–3\mu$. It is difficult or almost impossible, to determine the shape of particles smaller than $0{\cdot}8\mu$ in diameter, but all particles of this size and larger are found to be forms of the cubic system, principally hexagonal and triangular plate and tetrahedra. Since there is no sharp break in the properties of an emulsion at any particlar size of particle, it is probable that even the smallest particles are crystalline. There is no evidence of the existence of amorphous silver bromide. When crystals of silver chloride are grown from an ammoniacal solution, cubes are formed, if gelatin is present there seems to be a tendency for the 1.1.1 faces of the crystal to develop. The simple cube does not seem to be formed in the presence of gelatin.

When light shines on the silver halide a red coloration is produced. Luther showed that the halogen was liberated, and that the reaction did not take place if the pressure of halogen present exceeded a certain equilibrium value depending on the intensity of the light. These coloured halides are often called photohalides, they may also be prepared by subjecting a mixture of finely divided silver and silver halide to a high pressure. It was formerly considered that these photohalides consisted of silver subhalides. The work of Sichling, Lorenz und Eitel, and Lorenz und Hiege has, however, conclusively proved that these photohalides are colloidal solutions of silver in the halide. Sichling showed by E.M.F. measurements that if silver subbromide existed at all in the halides, it was only to a very small extent, and was only stable over a very short range of concentration. The existence of colloidal silver in the photobromide of whatever composition was definitely established. Lorenz and his co-workers showed that optically clear silver halides may be prepared by treating the fused salt with the halogen. When these optically clear crystals are exposed to light they darken, but remain at first optically clear, later the surface at which the beam enters becomes brown and the particles become visible in the ultra-microscope. The particles grow rapidly in the light, and will continue to grow if they are removed from the light and heated to 350° C. Heating without previous exposure to light does not produce these particles. The growth of these particles is accompanied by a diminution of coloration in the immediate neighbourhood. The effect is evidently due to the separation of colloidal silver in the metallic form. The analogy between these fogs and the metallic fogs formed in fused salts seems to be complete. It is probable that the latent image in the photographic plate consists of a colloidal solution of silver in the halide, and is the first stage of the formation of the photohalide. Many theories of the latent image have been put forward, among which may be mentioned that of H. S. Allen, who has suggested that the latent image is due to the loss of an electron by a molecule of the silver halide and the electron remains embedded in the gelatin. Under certain circumstances the electron may get back and the latent image may be destroyed. This, and many other theories have never been put to the proof. Some-

times it is difficult to devise experiments which will decide between various theories, all of which have been made as wide and indefinite as possible and consequently of little practical use. A deeper knowledge of the latent image can only be obtained by further experiments to test the various theories.

When silver bromide is precipitated by the addition of a soluble silver salt to potassium bromide in the presence of gelatin a colloidal solution is obtained. If the concentration of the silver salt added to the gelatin solution of potassium bromide is strong, the resulting colloidal solution appears blue by transmitted light[25], [26], [27]. Such emulsions are sensitive to red and even infra-red light. In the ordinary way emulsions are prepared from a dilute solution of silver nitrate, the emulsion thus obtained appears red by transmitted light. On ripening the colour changes to green. We do not know the size of the particles in the blue emulsion, they are probably very small. The red emulsion contains particles up to about $0 \cdot 1\mu$ in diameter, the green emulsion contains particles from $\cdot 5\mu$ upwards. In the blue and red emulsions the colours are quite well accounted for by the Rayleigh theory of the scattering of light by small particles, but as yet there is no explanation of the cutting off of the red end of the spectrum by the emulsions with particles of about the diameter of a wave-length of light. Keen and Porter have shown that a similar colour change takes place in a suspension of sulphur when the size of particle becomes a little greater than the wave-length of light.

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### *Colloidal Silver and the Colour of Silver Deposits.*

Colloidal solutions of silver in the finest state of division are yellowish brown in colour and as the size of the particles is increased the colour changes to ruby red, lilac, and blue. When these solutions are precipitated by the addition of an electrolyte a dark grey precipitate of silver is obtained. If a soluble silver salt is reduced by a powerful reducing agent such as alkaline pyrogallic acid, silver is precipitated in the black form, if a less powerful reducer such as pyrogallic acid alone, is used, a grey precipitate is obtained[1].

Any circumstance which tends to prevent the coalescence of the reduced silver such as the reduction of an insoluble salt, or the enclosure of the salt in gelatin, yields the dark modification. Collodion does not hinder the coalescence of the silver particles to nearly the same extent as gelatin[1].

The colour of the image obtained varies to some extent with the developer used. If gaslight paper is developed with an excess of bromide in the developer the first image becomes red, but appears black as the develpoment proceeds. The products of oxidation of some developers stain the gelatin yellow or brown as these oxidation products are present in the greatest concentration at those parts of the plate which have been most exposed, the silver deposit in the negative appears to be stained through, though this is not the case.

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### *Gelatin.*

In the dry plate the gelatin is not only a protective colloid for the preparation of the emulsion, an adhesive substance for attaching the sensitive substance to the glass and a photochemical sensitiser of the silver halide, but it plays a most important part in development. Unless gelatin, or some other colloid, is present, strong reducing agents such as alkaline developers will reduce silver halides without previous exposure to light. In presence of gelatin, however, this reaction is extremely slow[1].

The oxidation products of developers usually tan the gelatin—make it less soluble so that an ordinary negative shows the pictures in relief. The parts containing most silver being lowest, and the clear gelatin projecting to the greatest height[5].

Sheppard and Elliot have given an explanation of the reticulation of the surface of photographic negatives. Their explanation is based on Procters' work on the effects of acids and alkalis on the swelling of gelatin[10].

The colloid chemistry of gelatin is discussed in detail by Procter in the First Report. The most important later work on the subject is that of C. R. Smith, who has studied the mutarotation of gelatin[11]. He showed that gelatin in solution may be in a sol form A, stable above 35° C., or a gel form B, stable below 15° C. Between these two temperatures the two forms eventually come into equilibrium and this causes mutarotation. Form B is much more viscous than form A, and a certain definite concentration of B is necessary to produce gelatinisation. The authors' experiments show that probably two molecules of the A form combine to form one molecule of the B form.

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### *Gum.*

Gum is used in the gum bichromate process as the base of a pigment process just as gelatin is used in the carbon process, but a very thin layer of the colloid is used so no transfer is necessary. The gum is made insoluble by exposure to light after sensitisation with a bichromate. Gum arabic is generally used in this process. Starnes states that better results are obtained by the use of gum senegal.

Starnes has made some experiments from which he concludes that when bichromate is added to the gum it is at once rendered less soluble. On exposure to light it first becomes quite soluble and then, on further exposure more and more insoluble. Thus in the early stages of printing there is a reversal of the image. The phenomenon has, however, not been investigated quantatively.

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## COLLODION IN PHOTOGRAPHY.

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The use of collodion has been coincident with the rise and progress of photography—by collodion is here meant a solution of pyroxylin in ether alcohol.

Any discussion of the colloid chemistry of collodion apart from other forms of nitro-cellulose is almost an impossibility, for although a great volume of work has been done, only a very small part of this may be claimed as appertaining solely to collodion.

The role of collodion in photography is similar to that of gelatine. It acts as a protective colloid, as a support, and also at times plays a part in the actual reactions. The greatest difference between collodion and gelatine is that collodion, except to a negligible degree, does not act as a sensitiser. Its insolubility in water, comparative

indifference to temperature, and its chemical inertia, are in marked contrast to gelatine, and are the main characters which render it of such importance as a support. Any discussion of the photo-chemical reactions involved in the preparation or utilisation of collodion plates or papers would be redundant, as they are of the same general character as occur in all photographic processes, and are dealt with elsewhere.

A very full account of the history and preparation of collodion and its application to photography will be found in Vol. 2 of Worden's "Nitro-cellulose Industry," 1911, pages 827 to 897, where copious references are given to both patents and literature.

Very little exact information exists as to the specific characteristics of photographic collodion. It is obvious that the character of any solution will depend upon the nature of the nitro-cellulose used, the solvents being under comparatively perfect control. The exact nature of the nitro-cellulose depends upon two factors, namely, the raw material used for nitration, and the constitution of the resultant nitro-cellulose, which latter naturally depends upon conditions and details of the nitration process. The permissible nitrogen content for the production of a photographic collodion lies somewhere between 11 per cent. and 12 per cent., and generally about 11·5 per cent. It is found that quite small variations of nitrogen content may involve large variations in physical character, such as, refractive index, viscosity, water compatibility, &c. Hence the mere nitrogen content, within the limits mentioned, does not in any way constitute a guide as to the suitability, or otherwise, of a nitro-cotton. Many attempts have been made to devise methods which would yield more positive results, but with comparatively small success; the behaviour of the nitrated fibre towards polarised light has been investigated by several workers, and a rough indication of the degree of nitration of the cotton can be obtained in this manner. The greatest value of the method so far is that it clearly differentiates, first, unnitrated fibres; and second, fibres of varying degrees of nitration. It is now realised that the usefulness of polarised light will be greatly extended when the results obtained by its use are correlated, not only with the nitrogen content, but with the physical properties, such as viscosity, refractive index, &c., which are of much greater significance than the nitrogen content in determining the properties of the collodion as far as its photographic utility is concerned.

The lack of knowledge as to the constitution of the nitro-cellulose molecule is a bar to more exact information regarding the behaviour of nitro-cellulose solutions, as collodion, in the various processes for for which it is used in photography. Results of an anomalous character are frequent in all investigations, and although there is now available a large volume of observations, they cannot yet be exactly correlated, nor is the information available which explains their occurrence. The effect of drying the cotton before nitration, and especially the temperature and treatment to which it is subjected before the actual nitration takes place, has a profound influence on the physical properties of the resultant nitro-cellulose. Further, both time and temperature modify the nitrated cotton. It would appear that all nitro-cottons undergo a process of denitration to a

greater or lesser degree, and that this denitration explains the anomalies that are so frequently met with in connection with the viscosity of collodions, and also with the behaviour of different films from one and the same solution. This decomposition is capable of acceleration not only by temperature but by many chemical agents; and also, probably takes place spontaneously at ordinary temperatures. The action of bromides in causing denitration is well known. One aspect of this phenomena is its importance in relation to the question of the keeping properties of collodion plates and papers, and of the permanence of the photographic image, whether negative or positive after the usual processes of development, fixation, &c., and in this direction much further investigation is called for.

## CELLULOSE ESTERS.

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The technical problems which arise in any colloid industry naturally depend on the uses to which the finished material is put, and in view of the varied nature of the applications of such products as leather, glue, starch, explosives, and colloidal metals, it is not surprising that each industry is concerned with a somewhat different aspect of the chemistry and physics of highly disperse matter.

The industry of the cellulose esters has for its principal object the manufacture of a material of valuable mechanical properties. Its colour, transparency, surface, &c., though of great importance, would be of little moment if the material did not possess elasticity, tensile strength, and toughness at ordinary temperatures, and plasticity at higher temperatures. The object of the industry is the provision of a material combining these properties without prejudice to its adaptability for artistic and imitative effects.

It must be admitted that in the case of celluloid a high standard of technical excellence has been reached without the assistance of theories of the nature of the plastic material. The reproduction of material possessing the desired properties is accomplished only by strict control of the raw and semi-manufactured material, and close adherence to the conditions ascertained by experience.

A brief account of the manufacture of celluloid will be found in Thorpe's "Dictionary of Applied Chemistry,"[1] to which the reader is referred. The manufacture of plastic materials from acetyl cellulose is described by Worden.[2] The colloidal problems encountered in the two manufactures are very similar except in the case of the preparation of the starting materials, nitro-cellulose and acetyl cellulose. These will be considered separately.

Nitro-cellulose is made, as is well known, by the action of a mixture of sulphuric and nitric acids on cellulose, usually in the form either of cotton or paper. The two phases, solid cellulose and liquid acid mixture, persist throughout. It has been shown by Cross, Bevan, and Jenks, and by Hake and Lewis,[3] that there is an intermediate formation of sulphuric esters of cellulose, which are gradually converted

almost entirely into nitric esters. Leaving this complication out of account, however, it is evident that the reaction must proceed by the diffusion of the acid mixture through the fibre. The final degree of nitration reached depends principally on the composition of the acid mixture, and nitrocelluloses of all percentages of nitrogen from 10 to 13 occur in commerce. From what has been said it is evident that the nitration process is very complicated, and it is not to be wondered at that it has not been brought to mathematical expression, although a vast amount of data has been accumulated[4]. However, by the accurate control of the composition of the bath, the purity and humidity of the cellulose, the temperature and time of nitration, very uniform products are obtained, and, to take only one instance, that of the manufacture of guncotton, the accuracy of modern musketry and artillery practice proves how uniformly a two-phase reaction can be controlled, although involving diffusion through a membrance which itself alters during the reaction[5].

Acetyl-cellulose is prepared by the prolonged action of acetic anhydride, acetic acid and sulphuric acid on cellulose, but the process differs from nitration in that the product is soluble in the reaction mixture. In this case, therefore, the acids reach the cellulose by diffusion through a gel of acetyl cellulose in acetic acid. The final product of the reaction is homogeneous, at any rate down to ultra-microscopic limits, and the acetyl-cellulose is recovered in the solid state by precipitation with water. The acetylation of cellulose takes much longer than nitration, and up to the present the uniformity of the product is inferior to that of nitrocellulose. This is probably due partly to the difficulty of temperature control, and partly to the complications introduced by modifications designed to produce material soluble in special solvents[6].

The central point in the manufacture of celluloid and acetyl-cellulose plastic materials is undoubtedly the gelatinisation of the base. Nitrocellulose retains the form of the original cellulose, although harsher to the touch. When it is kneaded with camphor and alcohol it is converted into a transparent gel, and the remaining processes of the manufacture merely consist in manipulating the gel while it is slowly hardening through loss of alcohol and part of the camphor. It is rolled out into sheets, pressed into blocks, sliced on a planing machine, and finally polished if required. The treatment of acetyl-cellulose is similar in principle, although different solvents are employed.

During the evaporation of the volatile solvents from celluloid in its seasoning or drying stage, there is a gradual loss in weight, diminution in volume, and increase in specific gravity. It may be noted in passing that the specific gravity of celluloid is of particular interest to the manufacturer of celluloid articles, since he buys the material by weight, and, in effect, sells it by volume. The relation of the loss of weight to the loss of volume was investigated by the writer in relation to another technical problem. The extreme cases would be that of: (1) a sponge-like structure which could lose weight without (apparent) loss of volume in which case loss of weight/loss of volume $= \infty$; (2) a structure which could shrink in volume without loss of weight,

in which case loss of weight/loss of volume = 0. On *a priori* grounds, therefore, any value for this ratio (which is the apparent specific gravity of the alcohol and camphor lost) might be expected. It was found in some careful experiments on a certain variety of celluloid in the final stages of drying that the ratio varied only from 0·82 to 0·91, the mean value for 28 samples being 0·87. This is the specific gravity of a solution of camphor in alcohol containing 42 per cent. of camphor by weight. Although these experiments do not prove that the shrinkage in volume of celluloid while seasoning is exactly equal to the volume of camphor and alcohol lost, they show that the difference, if any, must be small.

There is no more fascinating branch of the technology of cellulose esters than the study of solvents. Hundreds of substances and mixtures of substances are known which have more or less marked solvent action on nitrocellulose or acetylcellulose, but the question of how to make a fair comparison between one solvent and another has never been completely worked out. The work was begun for nitrocellulose by the late F. Baker[7]. He came to the conclusion that the best solvent of a particular sample of nitrocellulose was the solvent which yielded the solution of lowest viscosity, and this is in agreement with manufacturing experience. It may be pointed out, however, that another method might be chosen, and that is to find the solvent yielding solutions which will bear the greatest dilution with an indifferent, miscible non-solvent, such as petroleum ether, before the cellulose ester is precipitated. This method is also in line with the technical valuation of solvents, and a rigorous comparison between the two methods would be most interesting. Petroleum ether has been suggested here as the indifferent liquid, because of the unexpected results sometimes obtained when mixtures of liquids act on cellulose esters. It has been long known that ethyl alcohol and ether are, separately, non-solvents of soluble nitro-cotton, but form a solvent when mixed. This mixture was investigated by Baker[8], and he concluded that the solvent power was exerted by a complex formed by the combination of ether and alcohol. This is a reasonable explanation of this particular case, but it does not explain the extraordinary effect sometimes produced on solvent power by the additions of quite small amounts of foreign substance. One instance which has long been known is the solvent power imparted to methyl alcohol by the presence of traces of acetone. A recent example of the technical application of the principle is Eng. Pats. 14,655 and 14,656[9], in which the addition of small quantities of substances such as nitro-toluenes, formanilide, &c., is employed to facilitate the solution of nitrocellulose in nitro-glycerine.

But, returning to the consideration of mixtures such as ether-alcohol where each constituent is present in bulk, it would be of interest to extend Baker's viscosity work on solvent power to such mixtures, and find what proportions of the constituents produced the best solvent mixture. Probably the records of such experiments exist, but they do not appear to have been published.—Index 9*a*. The results would be of value in a field somewhat remote from that of colloid chemistry, in view of the recent work of Bramley and others on binary

mixtures[10]. The viscosity/concentration curves of such mixtures usually show maxima, the positions of which vary with the temperature, and Bramley concludes that the viscosity of liquid mixtures as an independent test of compound formation in liquid mixtures is unsatisfactory. The writer suggests that the viscosity/concentration curves of mixtures of liquids containing a constant weight of a viscous colloid in solution might give more useful results. The viscosity of the solvent would be masked by the viscosity due to the colloid, dissolved, presumably, in a complex of the two liquids. It is certain that in many cases minima would be found, and it would be interesting to see whether these minima also shifted with change of temperature, and whether their position corresponded with molecular addition compounds. The method could be applied to all mixtures possessing solvent power for a viscous colloid, whether the constituents separately were solvents or not. For instance, mixtures of aliphatic alcohols and benzene hydrocarbons should be examined with nitrocellulose in solution, and mixtures of aliphatic alcohols and chlorinated paraffins with acetylcellulose in solution, and so on. Although the results obtained would be chiefly valuable as a contribution to the study of binary mixtures, they would also be useful data in the chemistry of emulsoid solutions[10a].

The same question was encountered in a different form some years ago by the writer in a purely technical investigation. It is well known that ethyl alcohol and toluene together form a solvent for nitrocellulose of low nitration. To find the composition of the best solvent, constant weights of nitrocellulose of imperfect solubility were treated with a constant volume of toluene and alcohol in different proportions and the amount of nitrocellulose dissolved by each mixture was estimated. The results showed that the optimum mixture corresponded closely with a mixture of three molecules of alcohol to one of toluene thus suggesting the existence of a complex $C_7H_8$, $3C_2H_5OH$. Regarded from the purely colloid point of view, perhaps, the development of solvent power by relatively small additions of other substances to partial or non-solvents is the more interesting owing to its analogy to organised processes such as nutrition.

The nature of the solid camphor-nitrocellulose complex is still unknown. Schüpphaus[11] believes that there is some kind of chemical combination between camphor and nitrocellulose, chiefly on the ground that the heat of combustion of celluloid is less than that of its constituents. But this is only the complement of the fact that camphor and nitro-cellulose evolve heat when mixed, which cannot be regarded as evidence of chemical combination. The large changes in surface energy which must accompany gelatinisation would be sufficient to explain the thermal phenomena.

The optical rotation of an acetone solution of camphor and nitrocellulose is equal to the sum of the separate rotations of the camphor and the nitrocellulose, within the limits of experimental error[12].

Dubosc[13] expresses the following views on the constitution of celluloid. Celluloid is a "camphrogel" of nitrocellulose, camphor being the dispersion medium. In the process of gelatinisation

solid nitrocellulose absorbs camphor present in the liquid phase (camphor and alcohol), forming a mass of gel cells enclosing a pseudo-solution of nitrocellulose in camphor and alcohol. The subsequent rupture of the cells during kneading and loss of alcohol by evaporation, leads to an enormous increase in viscosity. There is, however, in the case of camphor celluloid, no separation of suspensoid or solid phase, such as may happen with some of the substitutes of camphor. This is shown by milkiness or opacity in the celluloid, by brittleness and lack of plasticity in the working. The plasticity of camphor celluloid on heating to about 80° C. is attributed to the formation of a liquid phase by fusion, diminishing internal friction.

Dubosc admits that experimental evidence in support of these views is meagre, but on the whole they appear reasonable. Exception might be taken to regarding camphor as the dispersion medium when it occupies only about one third of the bulk of the celluloid.

Speculations on the structure of cellulose esters and the plastic materials made from them inevitably lead to a consideration of the structure of cellulose itself. Cellulose has already been treated by other writers in these Reports[14], and a much-needed emphasis has been placed on its colloidal character. There are still chemists who write as if the elucidation of the structure of cellulose were a problem analogous to the determination of the formula of, let us say, brucine or dextrose. The underlying assumption appears to be that some day the suffix n in the formula $(C_6H_{10}O_5)$ n will be determined, and then, given a sufficiently large sheet of paper, the complete formula will be constructed. It must be admitted that this assumption has led to much interesting research[15].

It is only natural that chemists should attempt to assign definite molecular weights to the materials they handle. The tendency probably arises ultimately from the extraordinary developments of theoretical chemistry on the basis of Avogadro's hypothesis, culminating in the work of Vant' Hoff. It may not be out of place to point out that of all the materials that we wear, handle and consume, those to which the methods of Vant' Hoff can be applied are in a vast minority. Colloidal chemistry would be immensely simplified if it could be brought under systematic mathematical treatment, but in view of the vast differences in properties between the colloidal and crystalline states, it is unreasonable to expect to force colloids into the crystalline system. It is agreed on all hands that if cellulose and similar colloids have a definite molecule, its weight must be extremely large. But the larger the assembly of $(C_6H_{10}O_5)$ units becomes, the more difficult it is to imagine what forces would come into play to put a sudden stop to the process of aggregation. In view of the continuous nature of plant growth, it is not to be expected that there should be a definite limit to the size of the cellulose aggregate, any more than there is to the size of a honeycomb. The limit to the aggregation of $C_6$ units is probably set, not by internal chemical forces, but by external conditions such as atmospheric temperature and humidity, and the vital activity of the plant.—Index 14*a*. Wohler's synthesis of urea was hailed as breaking down the barrier between organic and inorganic chemistry, but crystalline substances like urea

are not typical of vital processes. It is always in a colloid medium that the phenomena of life are manifested[16]. Fischer's synthesis of the polypeptides comes much nearer to an imitation of vital processes, and there appears to be no chemical limit to the application of the reactions he employed.

A distinction should be drawn between efforts to determine the size of the cellulose molecule and experiments to determine the configuration of the $C_6H_{10}O_5$ units. It may be remarked in passing that there is no reason to suppose that all the $C_6H_{10}O_5$ units have the same configuration, and a quantitative conversion of cellulose to any particular sugar is unlikely[16a]. Pictet and Sarasin[17] by the dry vacuum distillation of cellulose obtained lævoglucosan, and Sarasin has suggested that cellulose is built up from this unit[18]. Owing to the drastic nature of the decomposition involved, the suggestion must be taken with some reserve, and Irvine has criticised it on other grounds[19]. It is interesting, however, to build up l-glucosan with the aid of tetrahedral carbon atom models, when it will be found that the carbon atoms 1, 2, 3, 6 and the oxygen atom are approximately in one plane, and the carbon atoms 6, 3, 4, 5 and the oxygen atoms 7 and 8 in another plane, approximately at right angles to the first plane (*see* formula in bibliography). The complex would therefore grow in three dimensions (an elementary detail which is sometimes overlooked), and groups and atoms would be brought into proximity in a way which would never be demonstrated by a diagram in two dimensions. One is tempted to speculate whether the insolubility of cellulose in water is due to this mechanical smothering of the hydroxyl groups by the growing complex, or even whether the hydroxyl groups really exist as such in solid cellulose[20]. Certainly any reaction which degrades the cellulose complex yields a product which will take up more water than the original cellulose, and even long-continued mechanical grinding will yield a sticky or pasty mass; from which it appears that increasing the surface of cellulose increases its solubility in water. On the other hand, the vulnerability of cellulose to esterification without profound hydrolysis militates against this view.

The chief contribution which the manufacture of celluloid makes to colloidal theory at the present time is in its insistence on the fundamental difference between emulsoids and suspensoids. There is a close connection between the viscosity of dilute solutions of cellulose esters, and the mechancial properties (or what is called in the rubber industry the nerve) of the solid product[21]. So far as the writer is aware, neither suspensoid nor crystalloid solutions possess any physical properties which can be correlated with the properties of the solid derived from them by evaporation. In crystalloid and suspensoid solutions we have free particles—ions, molecules, or aggregates—moving independently of each other in the dispersion medium. But in emulsoid solutions, as exemplified by cellulose esters, we find a manifestation, in a reduced degree, of the same forces that produce " nerve " in the solid form. Therefore the disperse phase cannot consist, at any rate entirely, of particles having independent existence in the dispersion medium. There

must be structure, and perhaps the most reasonable assumption is a form of network in three dimensions, the interstices being filled either with pure solvent or with solvent containing disperse phase in a lower state of aggregation. There are admittedly difficulties in such a hypothesis, *e.g.*, in regard to the equilibrium between the two concentrations co-existing[22]. This view of the viscosity of nitrocellulose solutions draws a distinction between them and the highly viscous solutions of such crystalline substances as cane sugar in water, which may be regarded as owing their viscosity to the presence of large aggregates consisting of molecules of sugar surrounded by attracted water molecules. This suggests another contrast between the two. The attraction of sugar molecule for water molecules is regarded as being related to the high solvent power of water for sugar and also to the high viscosity of the solution. In the case of cellulose esters, as we have already seen, the best solvent is regarded as the one which gives solutions of least viscosity.

In view of these considerations, a study of the transition from emulsoid to suspensoid solutions would be of great interest. It is well known that an alcoholic solution of mastic, if poured into water, yields a suspensoid solution of mastic. In a similar way a dilute acetone solution of nitrocellulose on dilution with water yields a suspensoid solution of nitrocellulose. From some incomplete experiments it appears that the gradual addition of water to the acetone solution, keeping the concentration of nitrocellulose constant, produces a gradual rise in the viscosity of the solution, both absolutely and relatively to the viscosity of the solvent, until a maximum is reached, after which the viscosity falls until it almost coincides with that of the solvent. The Tyndall effect becomes marked close to the position of maximum viscosity. On the network view of the structure of nitrocellulose solutions these changes would mean a stiffening and probably a shrinkage of the network as the percentage of water in the solvent increases, and finally rupture into free particles, possessing a refractive index sufficiently different from that of the medium to show the Tyndall effect.

Reference should be made to the analogy developed in text-books of physics between viscous stress in liquids and shearing stress in a strained elastic solid, according to which a viscous liquid is regarded as able to exert a certain amount of shearing stress, but is continually breaking down under the stress. The equation developed is $\eta = n/\lambda$ in which $\eta$ is the co-efficient of viscosity, n the co-efficient of rigidity, and $1/\lambda$ the time of relaxation of the medium, *i.e.*, the time taken for the shear to disappear from the substance when no fresh shear s supplied to it. This is a much more illuminating way of regarding the viscosity of liquids than the analogy with gases, since the viscosity of liquids, unlike that of gases, diminishes with rise in temperature.[23] But it is particularly suggestive in the case of solutions of colloids like nitrocellulose and rubber which depend for their value on their mechanical properties[23a]. In the case of celluloid, in particular, we are dealing with what is at ordinary temperatures an elastic solid, and it would be most instructive to follow up its properties from dilute solution to the solid state, both with and without the addition of

camphor. The intermediate zone would offer considerable experimental difficulties, but the ground has already been broken by Trouton and Rankine[24].

A complete examination of celluloid from this point of view would include the viscosity in dilute solution, gradually increasing the concentration until determination of Trouton's coefficient of viscous traction became practicable, and finally the rigidity, bulk elasticity, and tensile strength as the celluloid gradually lost its solvent. In all cases temperature effects would have to be studied, and the comparison of rigidity and viscous traction at various temperatures would be of particular value in the case of finished celluloid, while the data as a whole could hardly fail to throw light on the problem of the structure of viscous colloids.

## References.


[1] Vol. 1, p. 705 (1912 edition). The account given here is written by Schüpphaus.

[2] "Technology of Cellulose Esters," Worden, Vol. VIII.

[3] Cross, Bevan & Jenks, Ber., **34**, 2496; Hake & Lewis, *J.S.C.I.*, **24**, 374 (1905).

[4] *See*, for example, Lunge, *J. Amer. Chem. Soc.*, **23**, 527 (1901), and many others.

[5] Nathan, *J.S.C.I.*, **28**, 177 (1909). Note particularly (p. 185) the small variation in nitrogen percentage (from 12·95 per cent. to 13·05 per cent. in a year's work).

[6] *See* Miles, Eng. Pat. 19,330 of 1905, on the solubility changes induced by partial hydrolysis. An extensive list of patents is given by Worden, *J.S.C.I.*, **38**, 370 T (1919).

[7] Baker, *Trans. Chem. Soc.*, **103**, 1653 (1913). The viscosity of nitrocellulose in various solvents follows the empirical law $\eta=\eta_0\ (1+ac)^k$, in which $\eta=$ viscosity of solution, $\eta_0$ = viscosity of solvent, $c$ = concentration, $a$ and $k$ are constants depending on solute and solvent. The value of $\frac{d\ log\ \eta}{d\ c}$ is convenient for comparing different solvents.

[8] Baker, *Trans. Chem. Soc.*, **101**, 1409 (1912). From the viscosity concentration curves given by mixtures of ethers and alcohols, it appears that dissociation of the latter takes place in such mixtures, but this dissociation is probably associated with the formation of an ether-alcohol complex, and to this complex the solvent power of these mixtures for nitrocellulose is due.

[9] Eng. Pats. 14,655 and 14,656 of 1915. (Rintoul, Cross, & Nobel's Explosives Co., Ltd.) The additions are of the order of 0.1 to 1 per cent., and enable the mixture of nitrocellulose and nitroglycerine to be gelatinised without raising the temperature.

[9a] Since this report was written, an important paper on the subject has been published by Gibson & McCall, J.S.C.I., **39**, 172–176 T, (1920). They find that the composition of the ether-alcohol mixture of optimum solvent power depends on the nitrogen content of the nitrocellulose.

[10] Bramley, *Trans. Chem. Soc.*, **109**, 469 (1916).

[10a] Price (*Trans. Chem. Soc.*, **115**, 1116 (1919)) has shown that the abnormality of the volatility of cordite made with equal properties of acetone and ethyl methyl ketone is not due to any abnormality of vapour pressure or density of the mixed solvents.

[11] Thorpe, *Dictionary of Applied Chemistry*, loc. cit.

[12] Unpublished observation. Only dilute solutions have been examined.

[13] Dubosc, *Le Caoutchouc et la Gutta-Percha*, 9803–9808 (1919).

[14] 1st Report, King 20–38, Chrystall 82–84.
2nd Report, Harrison 54–61.

[14a] Gibson makes the same suggestion in a recent paper. *Trans. Chem, Soc.* **117**, 482 (1920).

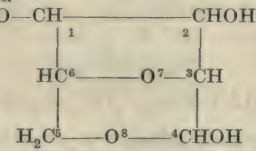
[15] *Cf.* Boeseken, v. den Berg & Kerstjens, *Rec. Trav. Chim. Pays Bas*, **35**, 320–345 (1916). Cellulose is regarded as $(C_6H_{12}O_6)n-(n-1)\ H_2O$, and the acetylation process is studied. As the molecule is hydrosed the acetyl number increases from 62·5 for cellulose triacetate to 77 for dextrose pentacetate. The molecule combines with $3n+2$ mols of acetic acid, giving a triacetate of molecular weight $(162n+18)+(3n+2)42$. The acetyl number $= \frac{1{,}000\ (3n+2)}{48n+17}$ from which $n$ can be calculated. Values of $n$ as high as 47·5 were found.

[16] The viscous colloids are nearly all of vital origin. *Cf.* gelatin, rubber, casein, the gums, etc.

[16a] *See* in this connection Miss Cunningham, *Trans. Chem. Soc.*, **113**, 173–181 (1918).

[17] Pictet & Sarasin, *Compt. rend.*, **166**, 38–39, (1918).

[18] Sarasin, *Arch. Sci. Phys. Nat.*, IV., **46**, 5–32 (1918). Starch and cellulose are polymerides of l-glucosan.



Polymers are found by the opening of the oxygen atom marked 8. This explains the presence of 2·5 dimethyl furane in the products of decomposition.

[19] Irvine, *Annual Reports* (*Chem. Soc.*), 69 (1918). The glucosan-polymeride formula is criticised on the ground that it does not account for the particular trimethyl glucose obtained from methylated cellulose by hydrolysis. (*See* Denham & Woodhouse, *Trans. Chem. Soc.*, **111**, 244 (1917)).

[20] Compton (*J. Franklin Inst.*, **185**, 745–774 (1918)), concludes that in the solid state, atoms are so intimately intermingled that particular molecules cannot be said to have any real existence.

[21] Eng. Pat. 114, 304 (H. Dreyfus) states that the higher the viscosity of cellulose acetates, the greater the amount of plastifying or softening agents which can be incorporated, and the stronger the resulting material from every point of view.

[22] In this connection *see* Bayliss, 2nd Report of this Committee. 'Protoplasm and Cell Contents,' and 'The Nature and Permeability of the Cell Membrane.' pp. 117–137.

[23] J. D. van der Waals, jnr. (K. Akad Amsterdam, Proc. **21**, 5 pp., 743–755, 1919) points out this difference between gaseous and liquid friction. He attributes liquid friction to the forces exerted by the molecules on each other, whereas in gases it is due to the transfer of momentum from one layer to another.

[23a] The resistance to shearing stress gradually increases as solvent is removed, until finally an elastic solid results.

[24] Trouton, *Proc. Roy. Soc.* **77**, 426 (1906) and Trouton & Rankine, *Phil. Mag.* [6], **8**, 538 (1904). In the stretching of rods of highly viscous material the following relation is found :—

$$\frac{F}{A} \Big/ \frac{dv}{dx} = \lambda$$

Where F = stretching force.
A = cross section of rod.
$v$ = velocity of given point of rod.
$x$ = distance of moving point from point of suspension.

From a chemical point of view it is unfortunate that Trouton worked with substances of so indeterminate a nature as pitch and shoemakers' wax. The use of a plastic material composed of a celluloid ester, a crystalline filler such as camphor, and alcohol, in a similar series of researches, would to some extent simplify the interpretation of the phenomena. We do not know yet why camphor is *par excellence* the solid solvent for nitrocellulose. It evidently possesses a somewhat unique combination of chemical and physical properties. Substitutes for camphor can only be accurately compared with it by some system of physical tests of the resulting material such as these. The explanation of its colloidal behaviour is not likely to be found until these experiments are done.

# COLLOID CHEMISTRY OF PETROLEUM.

*By* Dr. A. E. Dunstan.

A considerable body of evidence is available concerning the colloidal nature of crude petroleum and some of its distillates. Crude oil of the paraffin base type (*i.e.*, oil which on distillation yields solid paraffins in the high boiling fractions) usually contains colloidal amorphous matter which only assumes the crystalline state after distillation. It is probable that the effect of heat in this case is physical, bringing about a change of state whereby the wax is no longer in the dispersed condition characteristic of the original oil. Such oils and their residues after the removal of benzine and kerosene are frequently highly viscous, particularly at low temperatures, owing to the "setting" of the paraffin sol. This phenomenon may be demonstrated by immersion of a suitable residual oil in ice for several hours when the mass appears to be quite solid. A sudden jerk or violent shaking will destroy the quasi-solid mass and a thick clotted semi-fluid material will be formed.

The black or dark coloured "asphaltic base" oils contain bituminous matter which is to be regarded as being derived from the petroleum hydrocarbons by oxidation (and sulphuration) and condensation.

These oils are optically heterogeneous, although in most cases the degree of dispersion is very high (*see* Holde, *Koll. Zeits.*, 1908, **3**, 270; Schneider and Just, *Zeit. f. Wiss. Mikrosk*, 1905, **22**, 561).

The colloidal asphalts may readily be coagulated by means of strong sulphuric acid (Schultz, *Petroleum*, **5**, 205, 446). The chemistry of the well known "acid treatment" has been investigated by B. T. Brooks and I. Humphrey (*Jour. Amer. Chem. Soc.*, 1918, **40**, 822). The usually accepted view that olefines are polymerised to tar and removed as sludge is erroneous, for pure olefines (up to the $C_{16}$ member) do not give tars with acid up to 100 per cent. strength at 15° C. The formation of "acid tar" is probably a dual phenomenon—firstly, the acid coagulates the colloidal matter present in the oil; and, secondly, it brings about polymerisation of olefines and diolefines, sulphonation of aromatic derivatives, together with oxidation of primary materials and products.

Pyhälä (*Zeits. Chem. Ind. Koll.*, 1911, **9**, 209) considers that crude oils are sols of which the disperse phases are solid gels such as asphalt, together with liquid particles. Separation may be achieved by means of centrifuging or the addition of electrolytes. When the disperse phase exceeds 60 per cent. the phenomenon of gelatinisation makes its appearance.

In the discussion on a paper by Glazebrook, Higgins and Pannell (*Jour. Inst. Petr. Techn.*, 1915, **2**, 54 *et seq*) the writer brought forward the peculiar hysteresis effect in the viscosity of fuel oils and showed that by a suitable alteration in the previous history of a given oil, wide variations in its viscosity may be effected. The corresponding behaviour in aqueous gelatine sols is well known and affords an interesting parallel.

The colloidal asphaltic matter in crude oil and the yellow colouring matter in benzine, kerosene, and other distillates which is largely caused by "tar-fog" mechanically carried over, may be removed by coagulation (and solution) brought about by agitation with strong sulphuric acid. Direct adsorption on specific surfaces however, is equally effective. The writer has shown that floridin, Fuller's earth, and bauxite which, when freshly ignited, possess powerful adsorptive action, follow the well-known exponential adsorption rule :— $Y/m = ac^{\frac{1}{n}}$. For example, using a 0·25 per cent. solution of a crude asphaltic base oil in benzine as a test liquid, constant values of n were obtained and the Y/m — c curves were of the usual parabolic type.

The application of the adsorptive action of these substances in the refining of various distillates is well known and much of the theoretical side has been admirably expounded by Day and his co-workers (*Proc. Amer. Phil. Soc.*, 1897, 36, No. 154; *Trans. Petr. Congress, Paris*, 365; Gilpin and Cram, *U.S. Geol. Survey Bull.*, 365; Washington, 1908; and Gilpin and Bransky, *U.S. Geol. Survey Bull.*, 475, Washington, 1911. *See also* Richardson and McKenzie, *Amer. Jour. Sci.*, May 1910; Richardson and Wallace, *Jour. Soc. Chem. Ind.*, March 1912; Porter, *Bull.* 315 *U.S. Geol. Survey*, 1907).

In brief, the following conclusions were arrived at :—

(1) Fuller's earth tends to retain the unsaturated hydrocarbons and sulphur compounds in petroleum, thus exercising a selective action on the oil.

(2) When crude petroleum diffuses upwards through a column of Fuller's earth a fractionation of the oil occurs. The oil displaced by water from the earth at the top of the tube is lower in density than that from the bottom of the tube.

(3) The aromatic hydrocarbon in a mixture of a paraffin oil and benzene tends to collect in the lower end of the diffusion column.

Gilpin and Schnerberger (*Amer. Chem. Jour.*, 1913, **50**, 59) consider that the Fuller's earth behaves as a dialysing septum which allows paraffins and saturated hydrocarbons to pass freely but adsorbs bitumen, aromatic hydrocarbons, sulphur, and nitrogen compounds. The determining factor is surface. Similar views are propounded by Gurwitsch (*Petr.*, 1912, 8, 65) who ascribes Day's results not to capillarity but to specific surface adsorption. This author shows that floridin will adsorb solid paraffin from solution in petroleum spirit and benzol, but not from lubricating oil. An interesting observation was made by Herr (*Petr.*, 1909, **4**, 1284), who filtered Baku oil through fuller's earth and discovered that all the formolite forming compounds were removed, *i.e.*, the unsaturated compounds which react with formolin were adsorbed on the mineral gel.

It by no means follows that the compounds which are adsorbed can be recovered unchanged. Being possessed almost invariably of residual affinity the close contact afforded in the adsorbed layer promotes condensation and polymerisation, and thus Gurwitsch

(*Jour. Russ. Phys. Chem. Soc.*, 1915, **47**, 827) was able to show that floridin brings about active polymerisation when brought into contact with amylene and pinene, resulting in considerable rise in temperature. Curiously enough the same polymer, di-amylene, is produced both by sulphuric acid and by fuller's earth. Pinene, similarly, is converted after adsorption into sesqui and polyterpenes. Alumina behaves in the same way towards amylene, but is apparently without effect on pinene. The writer's experience has been that freshly ignited precipitated alumina is particularly effective as a decolourising agent for petroleum and its distillates and a series of experiments using a 0·25 per cent. solution of crude asphaltic oil in benzene showed the following order :—

| Material (1 gram). | c.c. of coloured solution decolourised. |
|---|---|
| Alumina | 60 |
| Fuller's earth I. | 30 |
| Bauxite I. | 30 |
| Bauxite II. | 25 |
| Bauxite III. | 20 |
| Ignited peat | 15 |
| Bone charcoal | 14 |
| Bog iron ore | 12 |
| Fuller's earth II. | 10 |
| Ferric oxide | 10 |
| Ball clay | 8 |
| Fuller's earth III. | 8·5 |
| Fuller's earth IV. | 4 |
| China clay | 2 |
| Kieselguhr | 2 |

The temperature at which the adsorbing surface exerts its specific effect is of some importance. Gilpin and Schnerberger (*Amer. Chem. Jour.*, 1913, **50**, 59) on passing Californian crude oil through fuller's earth found little fractionating effect at 20° C. but a satisfactory result at 70° C.

A peculiar observation made by the writer is of interest in this connection. Cold bauxite, which has been ignited and cooled in a vacuum desiccator was found to have lost its power of adsorbing sulphur derivatives from kerosene. When freshly heated (to 200° C.) its activity in this direction was regained. Heat appears to be evolved during active adsorption, thus a 20° C. rise in temperature was observed during the passage of 100 c.c. of kerosene through 50 grams of bauxite.

Amongst other effective materials may be mentioned Kambara earth (Kobayashi, *Jour. Ind Eng. Chem.*, 1912, **4**, 891), a mineral containing hydrated silica, which decolourises crude petroleum and adsorbs unsaturated hydrocarbons therefrom. Fibrous alumina has been recommended by Gawolowski (*Allg. Oesterr. Chem.*, 1908, **26**, 87), whilst animal charcoal and prussiate residues have long been employed for these purposes.

Naturally the degree of fineness of the adsorbent is important. The following case will illustrate this point :—

| Bauxite Mesh. | Activity. |
|---|---|
| 40/60 | 1·0 |
| 60/80 | 1·7 |

In point of fact the activity—all experimental conditions being the same—is approximately directly proportional to the mesh. A convenient method of demonstrating this point consists in treating a 100 c.c. of coloured solution (as *e.g.*, that already mentioned) with varying weights of decolourant, matching the filtered resultant solution with the standard solution in a Nessler jar (C. c.cs.) and plotting $\frac{100\ C.}{\text{mass}}$ against C. Ordinates at C = 50 give directly the reciprocals of the masses required to remove 50 per cent. of the colour. Thus with floridin :—

| *Mesh.* | Mass. |
|---|---|
| Passing 180 | 50/320 |
| Passing 80 and retained on 180 | 50/170 |
| Passing 20 and retained on 30 | 50/44 |
| and with Bauxite | |
| Passing 80 | 50/175 |
| Passing 60 and retained on 80 | 50/80 |
| Passing 20 and retained on 30 | 50/30 |

Little can be said as to the relationship between the chemical composition of the material and its adsorbent properties. Apparently hydrated silica or alumina is effective after combined water is expelled, but no general statement can be made. Substances giving the same analytical figures may behave quite differently, and again, bodies of dissimilar chemical composition may be equally effective as decolourising agents.

The essential feature of all effective adsorption agents is development of surface, hence mineral gels containing water of combination which, on ignition, possess a characteristic structure are decidedly likely to possess decolourising and desulphurising properties.

Very characteristic is the behaviour of bauxite (say, 40/60 mesh) on being gently agitated with kerosene or benzene. Apparently a process of peptisation goes on, for a considerable amount of very finely divided material separates in suspension in the petroleum, and is sufficiently fine to pass readily through filter paper (*see* W. Bancroft, Vol. II. Report on Colloid Chemistry, 1918, page 2 *et seq*).

A highly important contribution to the application of colloid chemistry to industry was made by Clifford Richardson (" The Modern Asphalt Pavement " and reprint of a paper read before the St. Paul Engineering Society, 1917). This investigator showed that the durability of anasphalt pavement is directly connected with the fineness of the mineral aggregate, *i.e.*, with the extent of the surface developed. The capacity factor of the surface energy is measured by the absolute surface displayed and the intensity factor by the particular surface tension of the materials employed. As a case in point, a

particular pavement laid in 1895, the surface of the aggregate was 44 square feet per lb. of material, whereas in a later one the surface was increased to 60 square feet per lb. The former pavement was unsatisfactory, and the latter was excellent.

Naturally occurring colloidal suspensions are found in Trinidad, where the asphalt contains 25 per cent. of finely divided mineral matter, but artificial mixtures of bitumen and dispersed clays can be made which may contain as much as 60 per cent. of mineral. The various asphalts (natural and artificial) possess different powers of retaining the disperse phase. Broadly speaking, asphaltic residues from crude oils are inferior in this respect to the natural bitumens.

*Mixtures of 67 per cent. Bitumen and 33 per cent. Clay (introduced while wet) and maintained at 325° F. for 24 hours.*

| Source of Bitumen. | Colloidal Matter. | | Sedimentation. |
|---|---|---|---|
| | Before heating. | After heating. | |
| | per cent. | per cent. | per cent. |
| Trinidad residue - - - - | 33·5 | 33·7 | 0·0 |
| Badabin ,, - - - - | 32·4 | 30·1 | 7·0 |
| Mexican ,, - - - - | 33·3 | 27·2 | 18·3 |
| California ,, - - - - | 31·8 | 23·8 | 25·2 |
| Mid Continental residue - - - | — | — | — |
| Semi-paraffin ,, - - - | 33·8 | 21·7 | 35·8 |

The temperature 325° F. is that at which is formed the film of bitumen which covers the mineral aggregate of a sheet asphalt pavement. It is striking that the Trinidad residual is so thoroughly differentiated from all the others, confirming the opinion based upon service tests in regard to the unique character of this material.

Although in actual refining operations the adsorptive properties of the materials described above have mainly been directed towards the removal of colour, yet considerable success has been achieved in connection with the equal important problem of desulphurisation. It by no means follows that an adsorbent is equally effective in removing colouring matters and sulphur derivatives. Usually this is not the case, and each material must be tested for its specific purpose. So far as the writer's experience goes, the sulphur compounds present in the lighter distillates are more readily adsorbed than those in the higher boiling fractions, although it is possible that in the latter case there is preferential adsorption of other substances, *e.g.*, unsaturated hydrocarbons. Whilst for example, floridin will desulphurise benzine quite readily, it has little effect on the sulphur compounds which occur in the lubricating oils derived from the same crude petroleum.

An interesting application of adsorption is to be seen in the method patented by Hall Motor Fuel, Ltd., for the purification of cracked

spirit. This material, as is well known, contains a considerable proportion of highly unsaturated hydrocarbons—olefines and diolefines —to the presence of which it owes its characteristic odour and its objectionable propensity towards resinification or "gumming." Although the reactive hydrocarbons can be removed by the agency of strong sulphuric acid, the operation is attended by serious loss, but by utilising the adsorbent capacity of floridin, the diolefines present are polymerised to high boiling products and a spirit free from objection is produced. The refining operation is best carried out with the spirit in the vapour state, under these conditions adsorption is followed by condensation and/or polymerisation.

Incidentally the sulphur derivatives present in many benzines and kerosenes may be removed in a precisely similar manner.

The problem of the breaking of persistent emulsions in refining operations is obviously one for treatment by the application of colloid chemistry. The soda wash which is employed to remove the traces of sulphuric acid in the refining of lubricating oils is a common source of this trouble and in some cases a practically permanent emulsion is formed. The sodium salts of naphthenic and sulphonated naphthenic acids are notable emulsifying agents and it is possible that hereinlies the cause of what is sometimes a serious difficulty. It is interesting to remember that sodium naphthenates are used very extensively as soap.

A recent patent by Southcombe and Wells brings out the novel point that a small amount (1 per cent.) of free fatty acid added to a mineral lubricating oil, not only replaces the usual blending fatty oil, but according as its molecular weight is low or high, yields a non-emulsifying or an emulsifying oil. It appears that the addition of the free fatty acid appreciably lowers the interfacial tension between the lubricating oil and the bearing.

Petroleum jelly or "vaseline" appears to be an emulsion of soft paraffins dispersed in heavy oils. The viscosity increases gradually with decreasing temperature until the gel state is attained, without, however, any separation of crystalline wax, but on being distilled, wax appears in the distillate. Various artificial jellies are on this market, being compounded of soft wax and heavy oil, these, on the contrary, are inclined to deposit crystalline matter on being cooled, and do not possess the salve-like nature of the natural product.* An apt comparison is in the different appearance of ice cream made with and without the addition of gelatine and in both cases—vaseline and ice cream—the presence of a protective colloid may be the explanation.

A peculiar illustration of the coagulation of a colloidal solution is seen in the action of flowers of sulphur on the yellow liquid which is produced by treatment of sulphur-containing distillates with sodium plumbite. There is a rapid flocculation and a dark brown precipitate appears.

* By this is meant the material which is obtained from a suitable crude oil by distilling off the lighter compounds and decolorising the residue (usually by filtration through fuller's earth).

The United States Navy Department and the Submarine Defense Association have developed a "colloidal fuel," and a summary of their report follows :—

"Pulverized coal can now be successfully held in suspension so that the colloidal liquid flows freely through the pipes pre-heaters, and burners of ships and power, heating and industrial plants equipped to burn fuel oil. Months after mixing, the composites show little or no deposits. A fixateur, which comprises about 1 per cent. or 20 lbs. per ton, acts to stabilise the particles of pulverised coal dispersed in the oil. In colloidal fuel every solid particle has its film of liquid hydrocarbon and a protective and peptizing colloid, itself combustible. These particles are in three classes as to dimensions—coarse, colloid, and molecular. By coarse is meant here the fineness of fifty million particles per cubic inch. The fixateur and fixated oil are readily made and may be shipped anywhere. The manufacture or distribution of the new fuels incorporating solid carbon in fixated oils involves no doubtful process or industrial problem. On burning, the combustion is so complete that with fair coal there is left no slag and very little ash, what there is being light as pumice and granular as sand.

"It is the property of colloidal fuel that without loss of efficiency per unit volume or change of oil storage or burning equipment it makes possible the conservation of at least 25 per cent. of the fuel oil now burned, or conversely with the oils now available in increases by 50 per cent. the world supply of fuel that is liquid. We may go further and state that a number of new fuels have been realised, each with varying percentages of oil and solid carbon. One useful composite, in the range of ordinary temperatures, is composed of about half coal and half oil. Another unctuous semi-liquid is nearly three-fourths coal and one-fourth oil. All the fuel pastes are mobile to sustained and easily applied pressure, and may thus be pumped, fed, and atomised in the combustion chamber. These semi-fluid composites will constitute the most compact and safest fuel for domestic and industrial use, and they will largely eliminate the smoke and ash nuisances of cities.

"For example, industrial colloidal fuel, grade No. 10, devised to use up some poor coal holding 25·5 per cent. ash, is composed of 61½ per cent. of pressure still oil, wax tailings, petroleum pitch and fixateur running 18,505 B.T.U. per lb. and 38½ per cent. of 'anthracite rice' running 10,900 B.T.U. per lb. This grade contains 162,500 B.T.U. per gallon, and has 10·2 per cent. of ash. The fixated oil itself had 151,750 B.T.U. per gallon. In fuel value, therefore, the colloidal fuel of grade No. 10 is worth 7½ per cent. more per gallon than the oil from which it is made.

"If instead of 'anthracite rice' very high in ash, a crude oil coke which is ashless had been employed, the colloidal fuel gallon would have contained 182,154 B.T.U., or roundly, 20 per cent. more than the oil base, and only quarter of 1 per cent. sulphur."

According to Wo. Ostwald (" A Handbook of Colloid Chemistry " page 103), petroleum oil fractions of high boiling point are to be classed as iso-colloids, *i.e.*, a category in which disperse phase and dispersion means possess the same (or analogous) chemical composition.

The ultra-microscopic examination of a number of mineral lubricating oils (Dunstan and Thole, *Jour. Inst. Petr. Tech.*, 1918, **4**, 191) has demonstrated that optical heterogenity exists, although, however, the degree of dispersion is exceedingly high. The same behaviour obtains for the fatty oils and it is possible that lubricating power is in some way connected with this iso-colloidal state.

Lubricating greases are examples of oil-water emulsions stabilised by soap. Commonly sodium soaps are used for motor greases and the proportions are lubricating oil (sp. gr. ·900–·910), 80 parts; stearin acid, 15 parts; and caustic soda, 2 parts. Part of the oil is mixed with the stearin acid and this is added to the soda in 40 per cent aqueous solution, with constant agitation. The remainder of the oil is then incorporated. Cheaper greases are compounded with lime soaps.

Acheson's oil-dag and aqua-dag are suspensoids of graphite in oil or water containing a protective colloid (tannin). Aqua-dag is made first, and the graphite is transferred from this to oil. The oil-dag contains about 15 per cent. of " deflocculated graphite " and is used in a dilute solution of lubricating oil (0·1 per cent. graphite) with beneficial results to the bearings, which gradually become coated with a " graphitoid " layer.

The colloidal graphite in oil-dag may be removed for analysis in two ways. Freundlich (*Chem. Zeit.*, 1916, **40**, 358) throws out the graphite by adding an electrolyte (acetic acid) to the benzol solution of the oil-dag whilst Holde (*Zeit. f. Elektrochem*, 1917, **23**, 116) adsorbs the graphite on recently ignited Fuller's earth in a Gooch crucible. A German proprietary material named " Kollag " appears to be similar to oil-dag.

The influence of colloidal bituminous matter which is mechanically carried over during distillation is frequently sufficient to prevent the easy separation of paraffin wax from that fraction known as " heavy oil and paraffin," and recourse is made to a sulphuric acid treatment before refrigeration. The paraffin scale is usually discoloured and contains a greater or less amount of uncrystallisable material which is removed by the process of " sweating," *i.e.*, fractional fusion. This operation serves to raise the melting point of the wax and also in part to purify it. Final decolourisation is effected by filtering the melted wax through Fuller's earth, bauxite, or prussiate charcoal.

## THE COLLOIDAL STATE OF MATTER IN ITS RELATION TO THE ASPHALT INDUSTRY.

*By* Clifford Richardson, M.Am.Soc. C.E., F.C.S. (*Consulting Engineer, New York*).

The presence of mineral matter in a high state of sub-division in a system solid-liquid, the latter phase consisting of asphalt, reveals some interesting phenomena, connected with the relation of surfaces of solids and films of liquids, particularly where the mineral matter is sufficiently subdivided to exist in a colloidal state as regards the

bitumen. Owing to the viscosity of such a continuous phase the particles of mineral matter with which it is associated may be regarded as a colloidal state, although they may be of dimensions which would prevent their existence in such a state with a more mobile liquid, such as water. Clay and finely divided silica present such a relation to a highly viscous liquid, asphalt for instance, which may be regarded as a colloidal one. Attention was attracted to the subject in the course of a study of the native asphalt found in the Pitch Lake in the Island of Trinidad, British West Indies. This deposit is unique from a geophysical standpoint. It exists in a crater of an old mud spring on the West Coast of the island, and at a distance of about half a mile from the Gulf of Paria. Its surface was originally 138 feet above sea level. Borings which have been recently made show that the crude asphalt exists to a depth of more than 175 feet at the centre of the deposit, which consists of a bowl-shaped mass covering, originally, an area of 114 acres. Specimens taken at various points on the surface and at different depths show that it originates in an asphaltic petroleum, derived from oil sands occurring at considerable depth below the lake, with which a paste of mineral matter and water, originating in a mud spring, has become associated by the churning action of the natural gas accompanying the petroleum, on the release of the pressure to which it has been subjected as the oil approaches the surface. The material formed in this way is of highly uniform composition in all parts of the deposit, and consists of an emulsion of bitumen with a paste of clay and fine sand, and has the following composition :—

| | Per Cent. |
|---|---|
| Bitumen | 39 |
| Mineral matter | 27 |
| Water and gas, volatile at 100° C. | 29 |
| Water of hydration of mineral matter | 5 |
| | 100 |

The water, which on melting the asphalt under certain conditions can be separated therefrom, in a somewhat concentrated condition, has been found to contain in solution large amounts of sodium chloride and sulphate with a considerable amount of ammonium and ferrous sulphates, together with borates and a readily recognisable percentage of iodides. It also contains smaller amounts of potassium, calcium, and magnesia salts. It is plainly of thermal origin.

*Refined Asphalt.*

As it occurs in the deposit it is known as crude asphalt. As such it is submitted to a process of so-called refining at a temperature of 325° F., which removes the water and results in a material known as refined asphalt, which has the following composition :—

| | Per Cent. |
|---|---|
| Bitumen | 57 |
| Mineral matter | 39 |
| Water of hydration of clay | 4 |
| | 100 |

In determining the percentage of bitumen in the refined material by means of solvents it is found that some of the mineral matter passes through the finest filters and is not removed from the solution on prolonged centrifuging. On examination under the ultra-microscope it is revealed that it consists of clay in a colloidal condition, originating in the mineral matter of the mud spring in which it existed in this state as regards the water with which it is associated, and which is introduced into the bituminous phase on the removal of the water on refining. The amount of mineral matter in the colloidal state depends on the concentration of the solution, that is to say, upon its viscosity, as shown by the following data :—

*Characterisation of Solutions of Trinidad Asphalt (T.R.A.).*

| Per cent. concentration. | Specific gravity. | Specific gravity increase for 1 per cent. (T.R.A.). | Absolute Viscosity of Solution. | Viscosity difference for 1 per cent. (T.R.A.). |
|---|---|---|---|---|
| Solvent : Benzol - | 0·876 | — | 0·00652 | — |
| 1 per cent. (T.R.A.)- | 0·877 | 0·0010 | 0·00654 | 0·00002 |
| 2 „ „ - | 0·879 | 0·0020 | 0·00687 | 0·00033 |
| 5 „ „ - | 0·883 | 0·0013 | 0·00759 | 0·00024 |
| 10 „ „ - | 0·889 | 0·0012 | 0·00961 | 0·00040 |
| 20 „ „ - | 0·911 | 0·0022 | 0·01629 | 0·00067 |
| 30 „ „ - | 0·930 | 0·0019 | 0·04198 | 0·00257 |
| 40 „ „ - | 0·957 | 0·0027 | 0·09477 | 0·00521 |
| 50 „ „ - | 1, 012 | 0·0055 | 0·31800 | 0·02240 |
| 100 „ „ - | 1·400 | 0·0076 | — | — |

*Characterisation of Solutions of Trinidad Asphalt.*

| Per cent. Concentration. | Refined, per cent. Colloidal matter. | Refined, amount calculated per 1 per cent. (T.R.A.). |
|---|---|---|
| Solvent : Benzol— | | |
| 1 per cent. (T.R.A.) - - - | 2·54 | 2·54 |
| 2 „ „ - - - | 2·01 | 1·00 |
| 5 „ „ - - - | 2·09 | 0·42 |
| 10 „ „ - - - | 2·73 | 0·27 |
| 20 „ „ - - - | 3·13 | 0·16 |
| 30 „ „ - - - | 4·19 | 0·14 |
| 40 „ „ - - - | 6·51 | 0·16 |
| 50 „ „ - - - | 10·69 | 0·21 |
| 100 „ „ - - - | 35·40 | 0·35 |

In dilute solution it appears that the amount of matter in a colloidal state is comparatively small, but with increased concentration, that is to say, with increased viscosity of the continuous phase, it

becomes progressively larger until in the refined asphalt itself all of the mineral matter, at ordinary temperatures, may be regarded as in a colloidal state. Trinidad asphalt appears, therefore, to be a material the components of which are in a state of equilibrium, and this accounts for its uniform composition. It is, therefore, a unique material, and it is to the large amount of surface energy developed by the highly divided mineral matter which it contains that the demonstrated industrial value of the asphalt is to be attributed.

*The Introduction of Colloidal Clay into the purer forms of Bitumen.*

In the light of the preceding facts the inference was drawn by the writer that clay in a colloidal state might be introduced in a similar manner, industrially, into the purer forms of asphalt, and into the residual asphalts prepared from petroleum. For this purpose, a paste of clay and water, in which the clay was in a colloidal state as regards the water, was emulsified with residual asphalts from various types of petroleum. The water was then driven off at high temperatures and it was found that the relation of the clay to the bitumen became a colloidal one. The proportions were so selected that the resulting material, after the removal of the water, should consist of 67 per cent. bitumen and 33 per cent. of clay. These materials were then maintained in a melted condition in tubes for 24 hours, at a temperature of 325° F. The sedimentation which ensued, with the reduction of the viscosity of the continuous phase at this high temperature, varied with the different residuals, and was as follows :—

| Source. | Penetration. | Per cent. Colloidal Matter. | | Per cent. Sedimentation. |
|---|---|---|---|---|
| | | Before Subsidation. | After Subsidation. | |
| Trinidad Residual - | 50 | 33·5 | 33·7 | 0·0 |
| Bababui „ - | 48 | 32·4 | 30·1 | 7·0 |
| Mexican „ - | 50 | 33·3 | 27·2 | 18·3 |
| California „ - | 50 | 31·8 | 23·8 | 25·2 |
| Mid-Continental Semi-Paraffin Residual. | 51 | 33·8 | 21·7 | 35·8 |

It is apparent from the preceding data that the colloidal capacity, if it may be so designated, of the different materials is characteristic of the particular bitumen and of its viscosity at a definite temperature. The various bitumens are, in this way, very plainly differentiated.

*Industrial Application.*

Industrially these observations are of importance, especially in the construction of asphalt pavements, such as that laid on the Victoria Embankment in London. The mineral aggregate of this surface consists of fine sand, a filler for the voids in the sand,

Portland cement, and the mineral matter afforded by that present in the Trinidad lake asphalt cement which forms the cementing or binding material of the surface. Experience has shown that the stability of such a surface under heavy travel is dependent on the amount of surface energy developed by the mineral aggregate, that is to say, by the state of sub-division of the particles composing this aggregate. While this will depend upon the size of the sand particles and of those composing the filler, it is also contributed to by the highly developed surface of the colloidal components of Trinidad asphalt and to an extent which would be entirely lacking if the purer forms of bitumen were used with the aggregate, a fact which has been demonstrated by the difficulties which have been encountered in the construction of asphalt surfaces with the residual pitches, free from colloidal mineral matter, which have been met with in the past decade in England, and which have necessitated the employment of various expedients to overcome them.

The relation of surfaces of solids to films of liquids, especially when the surface is developed to such an extent as occurs in material in a colloidal state, has been demonstrated, therefore, to be a matter of supreme importance in carrying out successfully the construction of asphalt roadways to carry intense traffic.

[NOTE.—A more detailed account of the colloid chemistry of asphalt is given in the following paper: 'The Colloidal State of Matter in its Relation to the Asphalt Paving Industry,' C. Richardson, Minnesota Engineering Society, May, 1917. W. C. McC. L.]

## VARNISHES, PAINTS AND PIGMENTS.

*By* R. S. MORRELL, M.A.Ph.D., F.I.C., *Chief Chemist, Mander Bros Wolverhampton.*

In spite of the importance of the problems of surface it is surprising that the scientific study of the class of products comprising varnishes, paints and pigments, has been so much neglected.

The primary components in some form or other, dissolved in a suitable liquid or a finely ground pigment incorporated with a medium as in a paint, introduce a field of investigation of great practical importance and of absorbing interest. If the medium contains water, as in water paints, the properties of ordinary emulsions are prime factors of success. Problems of viscosity arise in varnishes, paints, dopes, and coatings containing cellulose esters; moreover polymerisation of drying oils confers valuable properties on many varnishes and paints. The conditions of spreading on a surface depend on the physical properties of the components and of the mixtures. The changes on "drying" are essentially superficial, involving questions of adsorption, oxidation, and polymerisation, causing increases in viscosity. The permeability to water and the alteration in the appearance of films introduce the study of the properties of gels.

The resins in their many forms are typically colloid bodies, and their solutions show the properties of that class. The thickened oils

are considered by some to belong to the class of Isocolloids (Wo. Ostwald).

*Drying Oils.*

The drying oils used in varnishes and in paints in contact with water ought to behave like other vegetable oils in their power to yield emulsions, and the generalisations laid down in E. Hatschek's Report (B.A. Reports on Colloid Chemistry, **2**, 16), may be considered to apply. (*See also* "Modern Conceptions of Emulsions," W. Clayton, *J.S.C.I.*, **38**, 113, 1919.)

The drying oils seem to differ among themselves in their emulsifying power, although no drop number data are available. In the writer's opinion soya bean and linseed oils are superior to China wood oil; moreover, polymerised linseed oils emulsify better than raw linseed oil, but the emulsions are less stable. The properties of the emulsions with the soaps of the drying oils containing divalent metals are similar to those of other vegetable oils.

When a drying oil is thickened by heat out of contact with the air a marked increase in viscosity and modification of other physical and chemical properties are manifested. (The Chemistry of Linseed Oil, J.N. Friend, 1917, contains a full bibliography of the subject.)

Thickened linseed oil contains polymerised molecules, but there is also evidence of the shifting of the unsaturated linkages (Morrell, *J.S.C.I.*, **34**, 105, 1915). Such thickened oils are considered by Wo. Ostwald to belong to the Isocolloid class which includes petroleum, paraffin, liquid sulphur above 170° C., and highly polymerised liquids. (Wo. Ostwald, "Handbook of Colloid Chemistry," 2nd Edit., p. 102.)

The Isocolloids are considered to be composed of one chemical substance; in other words the disperse phase and the continuous medium contain the same substance in different states. Their internal friction shows remarkably high temperature coefficients varying greatly with changing temperature. Comparison with the system styrol-metastyrol is, perhaps, the best in considering thickened drying oils (Lemoine, *Compt. Rend.*, **125**, 530, 1897, and **129**, 719, 1899). Seaton and Sawyer (*Jour. Ind. Eng. Chem.*, **8**, 490, 1916), in an investigation on the molecular weights of drying oils and their polymers have found that only in stearic acid as solvent were they able to obtain values of the molecular weights which were independent of the concentration of the solution or which showed absence of combination of solvent and solute.

In view of the complexity of composition of linseed oil with its varying amounts of mixed glycerides more reliable results may be expected from China wood oil.

C. J. Schumann (*Jour. Ind. Eng. Chem.*, **8**, 5, 1916) has investigated the changes which Tung oil undergoes on heating. The oil at first forms a simple polymeride and on further heating it sets to a stiff gel. Schapringer (*Chem. Zent. Blatt*, **2**, 1469, 1905), considers that the gelatinisation proceeds in two stages, the first progressive, and the latter instantaneous; a case of mesomorphic polymerisation. (Kronstein, *Ber.* **35**, 4150, 1902, and **49**, 722, 1916.)

Fahrion considers that the polymerisation of wood oil is not analogous to that of styrol. Polymerised styrol, on further heating, yields styrol, but not so in the case of wood oil (*Farb. Zeit.*, **17**, 25, 83, 1912, and *Ber.*, **49**, 11, 94, 1916). Schumann concludes that a dipolymerised glyceride is first formed which has the power of forming molecular complexes under favourable conditions, giving an insoluble colloidal mass, not, however, accompanied by any further loss of double linkages beyond those diappearing in the first stage of the change.

The presence of decomposition products from the oil prevents the gelation; rosin has the same effect. The solid gel is stated to be transformable into the dipolymer on heating with rosin or with the decomposition products of the oil. It is stated that if the decomposition products of linseed oil are removed while the oil is heated linseed oil will gel rapidly. Schumann concludes that the polymerisation is mesomorphic.

The writer (Morrell, *J.S.C.I.*, **37**, 181, 1918) can confirm the formation of the dipolymer with its subsequent gelation, but he wishes to lay stress on intramolecular changes occurring during the heating of other drying oils; thus Cyclolin or Polyolin (solid polymerised linseed oil) is difficult to saponify, insoluble in amyl alcohol and is considered by de Waele to be of a ring structure (*Jour. Ind. Eng. Chem.*, **19**, 1, 1917).

Krumbhaar states that the speed of polymerisation of Tung oil constitutes the greatest difference between it and linseed oil, and agrees with Fahrion that the polymerisation product is partially soluble in the unchanged oil. The viscosity increases with the amount of the polymer until saturation is reached, when the polymer is thrown out. (*Chem. Zeit.*, **40**, 937, 1916.)

This property of thickening is only markedly shown by the more highly unsaturated oils of the open chain series. Union of molecule with molecule undoubtedly occurs and the polymeride remains dissolved in the liquid oil with increasing viscosity until the fluid coagulates. In the writer's experience half the oil has been polymerised short of the point of setting, beyond that point the mass consists of a gel of the dipolymeride whose viscosity is influenced by the presence of specific substances as in the case of gelatine in water.

The problems of polymerisation and of thickening of drying oils are of the highest practical importance. Further investigation of the Polyolin of China wood oil would throw light on the properties of the thickened oils, especially in their emulsions in water and in other media.

The formation and properties of linoxyn, the oxidation product of linseed oil, are those of a gel, due to oxidation and not to heat, as in the polyolins or cyclolins (Annual Reports of the Society of Chemical Industry, 1916–18). In the manufacture of linoleum (A. de Waele, *Jour. Ind. and Eng. Chem.*, **9**, 1, 1917, and M. W. Jones, *J.S.C.I.*, 1919, **38**, 26) four oxidation products result of which linoxyn is one. These differ in degree of oxidation and linoxyn may be considered as solid oxidised linseed oil. It must again be noted that the degree of unsaturation plays an important part, because olein gives no linoxyn

substance, although it contains unsaturated groupings. In oil varnishes the function of linoxyn is of paramount importance.

J. N. Friend (*Chem. Soc. Trans*, **111**, 162, 1917) has studied the effects of heat and of oxidation on linseed oil with reference to changes of density, viscosity, and coefficient of expansion. The problem is complicated by the decomposition of peroxides with the loss of water carbon dioxide, and organic vapours. There is an increase in volume up to the setting point of the oil, after which contraction ensues, and the expansion is dependent on the increase in weight. The contraction suffered by the linoxyn explains the cracking of old paint. The action of driers is bound up with the formation of peroxides. (Ingle, *J.S.C.I.*, **36**, 319, 1917, and Morrell, *Chem. Soc. Trans.*, **113**, 111, 1918.)

From the writer's experience the peroxides undergo polymerisation passing from viscid oils to varnish films. On exposure to air the peroxides undergo slow decomposition. (Ingle, *J.S.C.I.*, 1913, **32**, and **38**, 101, 1919, and Salway, *Chem. Soc. Trans.*, **109**, 138, 1916.)

The gelatinisation of drying oils and oxidation is a problem of the greatest importance affecting the protective power of coatings on wood and on metal. No doubt too much attention has been paid to the interpretation by changes due to modifications in composition or in orientation, but the distinctive and finer differences in the qualities of the coatings often find no explanation on strictly chemical grounds, and the investigator is driven to find some other cause. Many observers have noted the importance of the presence of the glyceryl radicle in the drying of an oil film although its presence has no marked effect on rate or amount of oxygen absorbed.

Primarily surface phenomena have to be studied and as yet no adequate help has been rendered by experience of other colloid systems. The writer has experienced this difficulty for many years, and is of the opinion that much can be learnt by closer investigation on the lines of study of the properties of gels. (Morrell, J.S.C.I., 1920, **39**, 153.)

In the changes occurring during the drying of oils attention must be paid to the surface action of the drier. Driers like lead and manganese are in colloid solution, and according to Wenzel's Law the amount of chemical change in unit time is proportional to the absolute surface. If it be granted that there is a large absolute surface in colloids many reactions will occur more rapidly and the phenomena of catalysis are especially marked in colloid systems.

Ostwald ("General Colloid Chemistry," p. 95) states that surface tension may be either raised or lowered by chemical action occurring in the two phases. A lowering of the surface tension between two phases would accelerate the reaction.

To the best of the writer's knowledge no such measurements in reference to linseed oil have been published. From his own experience from the measurement of the weights of drops in air by Morgan's method (*Amer. Chem. Journ.*, **33**, 1911), no change in surface tension of China wood oil before and after exposure could be observed. Possibly the linoxyn was insoluble because it

was necessary to filter the oil from an insoluble skin before the weight of the drops of the exposed oil could be determined.

The surface tension of lead drying oil against air is, however, lower than that of linseed oil, from which it would follow that the lead soap would tend to accumulate on the surface, whereby its specific surface would be increased and consequently its chemical activity.

The whole subject requires further investigation, and it is much to be deplored that so little attention has been paid to it.

*Varnishes.*

In a paper on the viscosity of varnishes, Seaton, Probeck, and Sawyer (*Jour. Ind. Eng. Chem.*, **9**, 35, 1917) state that varnishes show two types of solutions, viz., true and colloidal; they may, under certain conditions, show the Tyndall effect.

The suspensoid and emulsoid classes differ in viscosity characteristics. The systems consist generally of three components, resin, oil, and thinner, *i.e.*, resin incorporated by heat with oil and thinner added. The variation in the viscosity of the emulsoid type with change in concentration is very great. Seaton shows that the viscosity temperature curves (determined by the Doolittle method) of the true solution type, containing soluble gum and low in polymerised oil, are curves whilst varnishes containing highly polymerised oils give straight lines; moreover, determinations of the viscosity of varnishes at various temperatures will give information as to the nature of the varnish solution.

Decrease in dispersion increases viscosity in emulsoid colloids and addition of thinner, increasing the dispersion of the polymerised components, will lower it.

If Seaton's view is correct the viscosity temperature curve before addition of the solvent would be a straight line, but after addition of the thinner it would be a curve. The examples given by Seaton are striking, but a number of variables define the viscosity of emulsoid colloids besides concentration, temperature, and degree of dispersity (Wo. Ostwald, *Trans. Faraday Soc.*, 1913, **9**, 34); especially there is to be considered solvate formation where the viscosity increases with the amount of dispersion medium taken up by the disperse phase. In view of the difficulty in deciding with accuracy the amount and even presence of polymerised oils in varnishes such a relationship as indicated by Seaton is of great value. Similar changes in viscosity during ageing are of importance because unless the viscosity approaches a constant value in a month's time the varnish may become unsuitable.

The importance of viscosity measurement in the standardisation of aeroplane dope and aircraft varnishes has been fully recognised as a determining factor for flow and freedom of working of these coatings. In view of the variety of composition of varnishes the volatility of the thinner as affecting the flow is of considerable practical importance.

Varnishes often contain a disperse phase associated with the continuous medium.

The application of Hatschek's formula :—

$$\eta^1 = \eta \frac{\sqrt[3]{A.}}{\sqrt[3]{A-1.}}$$

$\eta$ = viscosity of the continuous phase.
$\eta^1$ = viscosity of the emulsion phase.
A = ration of total volume of the emulsoid to the volume of the continuous phase.

(*Zeit. Chem. Ind. Kolloid*, **11**, 284, 1912) would throw light on the relationship of resin, oil and thinner and also on the composition of the disperse phase, although the formula is stated to be inapplicable to organic solvents. Von Smoluchowski (*Koll. Zeitsch.*, **18**, 1910, 1916) does not consider the prospect of deducing such a formula likely to be successful.

The drying of varnish films is chemically an oxidation process accompanied by increase in weight, volume, and in viscosity during the formation of the colloid linoxyn. The rate of drying may at first be rapid, followed by a period of sweating or syneresis. After a time the sweating disappears; this is possibly a chemical process connected with movements in the combined oxygen of the peroxides primarily formed or to changes in the character of the preliminary linoxyn coating. Wolff (*Farben Zeit*, **24**, 1119, 1919) maintains that oxidation and polymerisation proceed at rates depending on the wave length of light to which a varnish is exposed.

It is to the linoxyn that the water-resisting power of varnishes is due. Recently work has been done in connection with the protection of metal and wood parts of aircraft under the auspices of the British Engineering Standards Association, and for the Materials Section of the Technical Department of the Air Ministry. Few resin or resin oil coatings are impervious to water; possibly Japan lacquer is the best.

From the writer's unpublished investigations the whiteness of a varnish layer when immersed in water is an emulsion of water in the resin oil mixing as continuous medium.

An emulsion would be formed if the emulsifying agent in this case, the resin or oil soap, forms a colloid solution in the non-aqueous solvent (Bancroft, *Jour. Phys. Chem.*, **17**, 501, 1913).

The best water-resisting coatings give an emulsion with difficulty, and although the layer may take up as much as 5 per cent. water, the varnish film will remain clear. The conditions are essentially dependent on the nature and concentration of the linoxyn surface layer and on the nature of the oil and rosin together with the electric charge on the metallic components present in the mixing. It must be pointed out that increased rate of drying of the oil is not sufficient to prevent emulsification.

The surface layer of a varnish is essentially semi-permeable to water, but not to salts contained therein, *e.g.*, NaCl, $K_2SO_4$, KCNS.

If plain wood be suitably varnished and placed in water absorption will proceed at a rate which varies with the nature of the coating. Professor Lang and the writer have found that for a high class article

the daily rate is 0·0003 grms. per sq. cm., and the rate appears to be the same either in a water-saturated atmosphere or when immersed in water. The absorption will continue without whiteness appearing until the wood is impregnated and the emulsion can form.

Similarly, gelatine under shellac will pull water through the film. If the film is in glass, cloudiness will appear at once in the absence of the absorbing undercoat, or if the layer is applied on an impervious surface. The milkiness disappears generally on drying the film. On continued immersion swelling ensues with the formation of blisters and detachment of the film.

Often the surface is ridged and shows numerous perforations as if the surface had been scratched and punctured, so that the water absorption on a glass plate becomes steady owing to complete saturation. The swelling must be due to the osmotic pressure of the colloid solution under the protecting layer of linoxyn compelling the compensating migration of water which forms the disperse phase of the emulsion.

It has been shown that normal solutions of NaCl, $MgCl_2$ and $CaC_2l$ prevent the whiteness of an ordinary varnish film and reduce largely but do not prevent the passage of water through the film.

N/2 solutions of the above salts have nearly the same effect, and this is true for solutions of $K_2SO_4$ and KCNS. There are slight differences in behaviour due to the nature of the metal, so that although sodium and potassium salts show the same behaviour yet magnesium is slightly different to calcium, and that again different to aluminium in the form of chlorides in normal and half normal solutions. In the case of calcium there is an indication of surface adsorption with the production of a surface bloom which can be rubbed off leaving a clear film. From the figures given by the Earl of Berkeley and Hartley (*Roy. Soc. Proc. A*, **92**, 477, 1916), it would appear that an osmotic pressure approaching 13·5 atmospheres is necessary to prevent the passage of water into a high-class ordinary outside varnish.

With the solutions of N/20 and N/200 of the above salts the water absorption increases largely, and attains its maximum in distilled water. The concentration of the linoxyn surface film together with polymerisation of the drying oil present appear to be factors deciding the impermeability; whereas the formation of the emulsion with the absorbed water depends on the nature of the emulsifying agent in the oil. (Morrell, *Jour. Oil and Col. Chemists' Assoc.*, **111**, 36, 1920.)

Sufficient has been given to show that in varnish films similar problems await solution as in ordinary emulsions, and the experience gained in researches on colloids in a water medium are of great value although the presence of non-aqueous solvents render many of the generalisations inapplicable.

Reference may be made here to some instances of application of knowledge gained by investigation of other colloid systems.

Bancroft (*Jour. Phys. Chem.*, **19**, 275, 1915) gives a number of instances of emulsions involving the use of varnish materials, *e.g.*, bronzing liquids in which the metal goes into the dineric surface.

Gelatine can be precipitated from a solution of glue by shaking with benzole, and rosin dissolved in dilute caustic alkali can be removed

by benzene (Winkleblech, *Z. Angew. Chem.*, **19**, 1953, 1906). Kerosene benzol, carbon disulphide, chloroform act similarly, but ether has no effect, and produces no emulsions. Such emulsions are noticeable in varnish analysis and are considered by Bancroft to be due to violent shaking, causing drops of the second liquid, which have the power of condensing colloid particles on the surface and coalescing to larger complexes, to form a rigid emulsion with water.

Colophony in the form of resinates behaves similarly to the soaps of fatty acids in forming emulsions. Among the more recent contributions to the subject may be mentioned the work of L. Paul (*Kolloid Zeits*, **21**, 176–91, 1917), who states that solutions of alkali and resin soaps behave like highly dispersed colloid systems. These colloidal soaps combine with basic dyes to form coloured rosin lakes and are characterised by the readiness with which they combine with petroleum hydrocarbons (*Z. angew. Chemie.*, **28**, Ref. 415, 387, 1915; and *Seifen Zeitung.*, **42**, 640, 659, 1915). The same author (*Kolloid Zeits.*, **21**, 148 and 191) finds that certain fractions of the distillate obtained by distilling a mixture of colophony with phenol or $\alpha$ and $\beta$ napthol yield dyes with diazo and tetrazo-compounds.

Just as in the case of fats, fatty acids, soaps, and tannic acid, the surface tension of water is lowered by resins or resinates which may be considered to assume emulsoid or suspensoid properties in different dispersion media. J. Friedlander (*Z. phys. Chem.*, **38**, 430, 1901) showed in the solution of rosin in 1 per cent. alcohol how very slight are the changes in viscosity of a liquid when it takes up a suspensoid phase, and again a solution of rosin in alcohol containing a little water possesses a relatively high temperature coefficient (5–6 per cent. per degree temperature) against that of water, 2 per cent. (Hardy, *Z. phys. Chem.*, **33**, 328, 1900). Cohn (*Chem. Zeit*, **40**, 791, 1916) describes gel formation produced when colophony is treated with aqueous ammonia.

A. P. Laurie and Clerk Ranken (*Roy. Soc. Proc. A*, **94**, 53, 1917) describe the imbibition exhibited by some shellac derivatives. The solid which separates on cooling a solution of shellac in boiling sodium carbonate when immersed in water expands rapidly and ultimately disintegrates to a flocculent precipitate. At the maximum point of expansion the solid on immersion in a solution of sodium carbonate contracts, expanding again when transferred to water. It was found that the expansion was inversely proportional to the concentration of the salt solution. Since the shellac molecule is here considered to be permeable to salt solutions the mechanism of the expansion may be accounted for by the passage of the salt solution through the diaphragm, the soluble nucleus dissolving in the presence of the salt solution and the amount which can dissolve controlling the consequent osmotic pressure.

Shellac films from spirit solutions do not absorb normal salts from half normal solutions. The writer (*loc. cit.*) has found that the presence of salts, *e.g.*, N/2 $K_2SO_4$ or N/2 KCNS reduces the water absorption of the shellac film and no salt could be detected passing through it. The water absorption by shellac is much less than in the case of ordinary varnishes, but the effect is more permanent giving a cloudy

layer which does not clear on drying and becomes very granular with eventual loss of cohesion. Like varnish films shellac gives a semipermeable membrane and with half normal solutions of salts the absorption of water is practically inhibited.

In a varnish film such an equilibrium would leave the film clear, but in shellac there is a persistent cloudiness indicating that the film is becoming granular. The examination of the properties of shellac films is of interest in comparison with oil rosin films. In some respects there is much in common, but in the impregnated shellac film, water is probably the continuous medium. As in the case of oil varnishes a certain per cent. of water can be absorbed without opalescence appearing.

Natanson (*Z. phys. Chem.*, **38**, 690, 1901) has followed up Poisson's researches of 1829 in which it was stated that when a liquid is subjected to deformation a certain time is necessary for obtaining equilibrium, different for different liquids. Liquids have a very small relaxation value. For castor oil from G. de Metz's results the relaxation time is 0·0031 secs., and for solutions of tragacanth and collodion, values of the same order.

Reiger (*Physik Zeitschrift*, 8, 537, 1907; and *Annalen der Physik*, 4, 31, 51, 1910) has shown that fluid mixtures of rosin and turpentine have a possible elastic reaction by an oscillatory viscometric method provided due allowance be made for surface forces.

De Metz (*Comptes Rendus*, **136**, 604, 1903) has examined the very slow relaxation in the double refraction of a copal varnish induced by mechanical deformation caused by pressure or extension. The phenomenon of relaxation in a varnish lasts long enough to be observed in the fall in the double refraction. $T = \frac{t - t^1}{\log \Delta - \log \Delta^1}$, where log is to base e and $\eta = nT$ (Maxwell, *Phil. Mag.*, 4, 25, 129, 1868). T = time of relaxation, $\Delta$ and $\Delta^1$ the difference of path of two rays at times t and $t^1$; $\eta$ = coefficient of internal friction of the varnish and n = modulus of rigidity.

The modulus of rigidity of a liquid varnish calculated on the above formula is $n = 0 \cdot 12 \frac{\text{dyne}}{\text{cm}^2}$ at 22° C., and is of the same order as that of gelatine in water calculated by another method (*c.f.* Schwedoff, *Jour. d. phys.*, **8**, 341, 1889, and **9**, 34, 1890).

### *Paints and Pigments.*

In the literature on oil paints the application of the principles of colloid chemistry is very scanty.

H. A. Gardner (*Jour. Ind. Eng. Chem.*, **8**, 794, 1916) discussing the physical character of pigments and paints, points out that the opacity of pigments generally increases with fineness of division. As the refractive index of the vehicle approaches that of the pigment the opacity diminishes. Hence, in turpentine and in linseed oil the opacity will be less than in water as those media have higher refractive indices.

A lead paint will be opaque since its refractive index is greater than that of the oil, whilst a silica paint in turpentine or linseed oil will be practically transparent owing to close equality in the refractive indices of pigment and medium.

The opacity varies inversely with the amount of oil absorbed by the pigment, but the durability is improved by the presence of more oil.

The refractive indices of silica, barytes, zinc oxide, white lead, and zinc sulphide are 1·55, 1·6, 1·9, 2·0, and 2·37 respectively.

In lithopone a mixture of the components fails to give the same opacity as when prepared in contact. Between the limits of 28 per cent. and 38 per cent. zinc sulphide the covering power is best. It is probable that surface adsorption of the zinc sulphide by the barium sulphate occurs.

Rapidity of precipitation, strength of solution and temperature control, are factors which aid in the production of fine grained particles giving the greatest opacity.

The phenomenon of surface adsorption shown by certain lake bases in the presence of colouring matters is of interest and explains why the highly colloid pigments are often preferred. A measure of the degree of dispersion might be based on their colour.

Bingham and Green (*Am. Soc. Testing Materials*, 1919) distinguish between the viscosity of true liquids and the rigidity of plastic solids.

The application of the generalisations drawn from the study of other classes of colloid bodies to problems of the paint industry are referred to by Bancroft ("Theory of Emulsification," V., *Jour. Phy. Chem.*, **17**, 501, 1913). The use of sodium silicate to give an emulsion with linseed oil to prevent the paint from setting or hardening in the package has been known from 1865. Generally 2 per cent. water is the limit, although 4 per cent. may be employed to prevent settling, provided the emulsification of oil with water is assured. Instead of water as combining medium a rosin oil mixing may be employed. An alkaline water fluid is not desirable, and the addition of zinc oxide to the lead white is useful in maintaining the suspension in the linseed oil.

E. E. Ware and Christman (*Jour. Ind. Eng. Chem.*, **8**, 879, 1916) recommend that a non-aqueous protective colloid, *e.g.*, aluminium palmitate or oleate should be added to mixed paints to which small quantities of water have been added containing a protective colloid to prevent settling of the pigment.

The same authors have investigated the skinning, puttying, and livering of mixed paints. Livering is dependent on the acidity of the pigment, and in the case of enamels must be connected with the gelatinisation of the colloid resin due to reduction of its acidity. The coagulation depends on many factors of composition and the presence of foreign substances. Such gels would absorb oil and thinner with separation of the pigment. Skinning would seem to be caused by the oil acids acting on the pigment.

In an oil paint containing rosin the formation of resinates increases the viscosity and the further formation of zinc soap separating from the viscous solution of zinc resinates gives a gel occluding or adsorbing

the remaining oil (livering). Under suspensoid pigments the adhesive properties and cementing values of paint pigments apparently increase with approach to colloidal form. All paint pigments have colloidal properties. Gardner found in the clear oil upon the surface of specially prepared pigments which had stood for a year, the presence of pigment material showing Brownian movement on thinning with benzols. Experiments made with zinc oxide and with silica ground in linseed oil (thickened) gave even after thinning with four vols of benzole a cloudy fluid which yielded no clarification on centrifuging, but could be partially clarified by mixing the two fluids, a change probably due to electric neutralisation.

Paranitraniline red in oil is clear and slightly coloured, becoming bright red when benzole is added, a colour change common in the case of many suspensoid sols.

Prussian blue shows strongly Brownian movement and many particles of chrome green suspensoids are coloured crimson, orange, green, and blue in the ultramicroscope.

Carbon black (containing 90 per cent. carbon) probably adsorbs linseed oil as in the case of pigments. In the presence of strongly oxidised or boiled oils precipitation may occur on addition of benzene, which may be due to imbibition of the spirit comparable with the swelling of rubber in benzene or of gelatine with water. Again, if zinc oxide or lithopone be ground in alcohol and linseed oil added, the alcohol is displaced probably due to lowering of surface tension by introduction of the oil.

[An excellent summary of the properties and uses of carbon black is given by Perrott and Thiessen (J. *Ind. Eng. Chem.* **12**, 324, 1920,).]

Ayres (*J.S.C.I.*, **35**, 676, 1916) considers that "foots" from raw linseed oil can be removed easily by heating to 100° C. and centrifuging.

The presence of the mucilaginous material containing salts is considered by some to be highly detrimental not only in the manufacture but in the durability of many mixings and paint coatings.

Ware and Christman (*loc. cit.*) conclude that the use of emulsifying agents in paint grinding to prevent hard setting has not been satisfactorily explained. The emulsifying agent must exert no saponifying action on the oil, but the presence of metallic soaps in certain quantity retards the settling.

Hurst and Heaton state that the emulsification of the oil requires to be assisted by metallic salts such as zinc sulphate, manganese sulphate, and borax, &c.; moreover the addition of a minute proportion of tannic acid incorporated with the pigment prior to grinding with the oil causes the deflocculation of the pigment (Acheson, *J.S.C.I.*, **30**, 1426, 1911).

Cellulose varnishes have already been dealt with in previous reports under nitrocellulose, celluloid, and cellulose acetate.

A class of varnishes containing synthetic rosins on a phenolic trioxymethylene basis is of growing importance.

[Annual Reports of the Society of Chemical Industry (Paints, Pigments, Varnishes, and Resins, 1916, 17, and 18) and G. Matsumato, *Jour. Chem. Ind.*, Tokyo, **18**, 434, 1915; *J.S.C.I.*, 1104, 1915.]

The synthetic rosins may be soluble or insoluble in alcohol depending on the conditions of manufacture and show a great variety of chemical and physical properties. Their composition is complex (Lebach, *J.S.C.I.*, **32**, 559, 1913). The preliminary substance is a phenol alcohol, $C_6H_4$ (OH) CHOH.

Bakelite discovered by Baekeland, consists of soluble and insoluble forms. On stoving alcohol-soluble Bakelite at 140°–170° it passes to a hard insoluble layer or lacquer or to a solid of high chemical and mechanical resistance (Bakelite C, Resite).

Resite has been considered to be derived from polymerisation products of $CH_2 : <\overline{\quad}> = O$ (Wohl, *Ber.*, **45**, 2046, 1912).

The advantages of further study of such synthetic organic colloids seem to invite inquiry. Viscosity, gelation, relaxation effects, and dielectric properties are of importance, and, with the exception of the latter, await investigation.

There remains one important class of varnishes, viz., the black japans and black varnishes with carbon black as base.

In general, the pitch base blacks ought to show similar behaviour to the resin mixings or to resin mixings containing no oil with allowance for the nature of the pitch (asphaltum or resin or stearine).

The knowledge of their properties is in the hands of the craftsmen and owing to the complexity of the mixings is of the nature of a trade secret.

Those on a carbon black base involve the knowledge of the properties of carbon black in non-aqueous media. The suspensoid black in a high degree of fineness adsorbing the continuous medium is assisted by an emulsifying colloid forming a membrane around the particle of black.

The results obtained from attempts to produce liquid fuel from petroleum and coal dust are industrially applicable in this case, but the presence of resin and oil gives a more favourable medium for holding the carbon black in suspension.

From the brief summary of a very scanty literature it will be evident that although the main properties are conditioned by the chemical composition of the components, nevertheless the properties which decide between a high and low class of article or between suitability or unfitness are rather to be looked for in a comparison of relationship of phases and in changes of surface energy and adsorption.

The author desires to express his thanks to Mr. P. J. Fay, M.A. for help in the selection and arrangement of the material for this report.

## CLAYS AND CLAY PRODUCTS.

*By* A. B. Searle, *Consulting Chemist, Sheffield.*

The details of the structure of clays and clay products are to a large extent unknown. This is due to the variety of the materials commonly known as *clays*, to the complexity of the reactions which take place when the clays are moistened, dried, and heated, and to the extreme difficulty in studying the products of the reactions.

There are numerous definitions of the term *clay*, but most of them are incomplete. Some are so inclusive as to be applicable to any plastic material, others involve an erroneous assumption as to the manner in which the "alumina" and "silica" are combined, and no definition has yet been published which is entirely satisfactory. Until a better one is forthcoming the following is convenient, though by no means free from objection :—

> A clay is a naturally occurring earthy material, whose chief physica characteristic is its plasticity, and whose essential constituents are reported in an analysis of the substance to be "alumina," "silica" and "water."

This definition does not exclude those highly siliceous and plastic materials commonly known as "brick clays" though some of these are known to contain as much as 60 per cent. of materials of a non-plastic, sandy nature, which is certainly not of the nature of clay.

When a commercial sample of clay is mixed with an equal weight of water and allowed to stand for a few moments, and the liquid decanted through a sieve having 200 holes per linear inch, this treatment being repeated with fresh water until all the small particles have been removed, the residue will usually be devoid of plasticity and will not possess the properties of clay. Usually, it will resemble sand or a mixture of gravel, sand, and rock flour. When some clayey materials, such as some indurated clays, are subjected to this treatment, the whole of the plastic material is not removed, but on prolonged exposure to water, or better still, if the water is made slightly alkaline and boiled in contact with the clay for several hours, the material will be effectively separated into a coarser, sandy, non-plastic matter, along with the smallest non-plastic particles. By a suitable modification of the treatment just mentioned, a "clay" may be divided into a number of fractions, of which all those consisting of particles which will not pass through a No. 200 sieve are obviously not clay. The finer particles are sometimes designated "clay substance," but, though they contain the whole of the plastic material, they are not wholly "clay," as by careful elutriation or repeated sedimentation a further series of non-plastic and siliceous materials may be separated. Seger[1] suggested that the particles which were carried away by a stream of water flowing at the rate of 0·18 mm. per second should be regarded as "clay substance," but this fraction contains a considerable proportion of non-clayey material unless it is derived from a particularly pure clay, so that this use of the term "clay substance" should be abandoned.

The smallest particles which are obtained by elutriating the materials commonly known as clays are found to correspond more or less closely, on analysis, to a composition which may be represented by the formula $H_4Al_2Si_2O_9$. In some samples of Cornish clay and some kaolins, the composition is remarkably constant, but many highly plastic clays and most fireclays yield a product richer in silica and deficient in the elements of water. The constancy of the composition of the better qualities of white-burning clays has led to the supposition that there is in all clays an essential substance—*true clay*, *clayite*, or *pelinite*—on which all clayey mixtures depend for their chief properties. The existence of this "true clay" has

been so often assumed that there is a widespread impression that it really exists as a definite chemical compound, though it has never been satisfactorily isolated. A further objection to this belief in the existence of a single substance as the essential ingredient of all clays, is the fact that the composition and properties—especially the plasticity—of the elutriated product differs with the origin and nature of the " clay " from which it is obtained. A further objection is that all attempts to obtain a pure product by chemical means or to produce a synthetic clay have failed.

It has also been suggested by W. and D. Asch[2] that the essential ingredient of all clays is not to be expressed by a single substance, but by a large number of substances, each of which have a general similarity in composition, but differing from each other in the arrangement of the atoms in highly complex molecules. Thus, all clays possess properties corresponding to those of a series of insoluble acids and may, therefore, be regarded as alumino-silicic acids. W. and D. Asch[2] go still further and suggest that the essential substances in all clays are alumino-silicic acids, the atoms of which are arranged to form several ring-compounds united together, each ring containing six atoms of either silicon or aluminum together with the requisite number of oxygen and hydrogen atoms (the latter being in the form of hydroxyl groups) to form a saturated compound. In most cases, two or more hydrogen atoms are assumed to be replaced by those of sodium, potassium, calcium, magnesium, or iron.

Asch's theory has been worked out in great detail with regard to the available evidence, but for its ultimate proof it requires the synthetic production of clays of various compositions and this synthetical proof has not yet been accomplished. The synthesis of silica in the form of a hexagonal ring compound, $Si_6O_{12}$, by G. Martin[3] in 1913 lends some support to the suggested constitution of the purer clays. It has also been suggested that plastic clays are compounds of " alumina " and " silica " with organic groups. This theory does not appear to have been very fully investigated. It has the disadvantage of being largely inapplicable to the purer kaolins which are almost devoid of organic matter.

It was, at one time, thought that the plasticity of clays is due to the presence of bacteria and bacterial products, but this has not been proved, and appears to be improbable.

Although there is a considerable amount of evidence of the existence of one or more definite chemical compounds which are the essential ingredients of clays and, therefore, to be regarded as " true clay," there are numerous properties of clays which cannot be explained by any purely " chemical " theory, and of these the most important is the plasticity. There are also properties which are capable of other explanations, particularly those based on the colloidal nature of clays.

The existence of colloidal matter in clays was first established by Th. Schloesing[4] in 1872, but the most systematic exposition on the colloidal properties of clays is that of P. Rohland[5] in 1891, and more recently the possession of colloidal properties of clays has been generally recognised[6].

At the present time, the most probable theories of the constitution of clays are as follows :—

(*a*) Clays are a mixture of adventitious minerals (such as sand) and one or more alumino-silicic acids, the latter being the true clays.

(*b*) Clays are adventitious mixtures of an inorganic colloidal compound, or of several analogous compounds, and of inert minerals such as sand.

(*c*) Clays are mixtures of alumina and silica or other simple mutually precipitated colloids with other non-colloidal minerals, such as sand.

A little consideration will show that (*a*) is not necessarily incompatible with either (*b*) or (*c*), as the two latter do not give any indication of the chemical composition of the colloidal matter. Moreover, (*c*) is not applicable to all clays, though it may be to some, so that present-day views of the constitution of clays may be reduced to regarding them as mixtures of non-clayey material (sand, &c.), with either (1) a complex compound possessing colloidal properties, or (2) a mixture of colloidal silica and alumina.

There is evidence in support of both these theories and no comprehensive combination of both of them has been published, yet neither theory alone explains all the facts, unless it is sufficient to regard the first theory as applying to some clays, whilst the second is more applicable to others.

It appears quite certain that commercially useful clays are not wholly colloidal in character; they rather resemble a mass of mineral particles, each covered with a film of colloidal matter. If the latter could be wholly separated, it would not possess all the properties which make a clay technically useful, and in this respect the application of the term *clay* to mixtures of sand and colloidal matter would appear to be justified. The laterite clays which are widely distributed in the tropics, are characterised by a large proportion of alumina and silica soluble in hydrochloric acid. The ratio of these two oxides is very variable, and seldom reaches 1 : 2 which is a conspicuous feature of the purer British clays. This great variation makes it more probable that the laterite clays are merely mixtures of colloidal silica and alumina; their other properties resemble those of such a mixture rather than those of typical clays, and the conclusions based on the results of elutriation may require to be received with caution.

The proportion of colloidal matter which can be definitely separated from clays is extremely small, being less than 3 per cent.[4] in the most highly plastic specimens.* Many investigators find it difficult to believe that so small a proportion can account for such great differences in the behaviour of lean and highly plastic clays, and have urged this as an argument against the plasticity of clays being due to the colloidal material present. On the other hand,

* Ashley[7] has proposed to determine the relative amounts of colloids in clays by observing the amount of each required to just decolourise a standard solution of malachite green. This method, whilst useful for comparative purposes, gives no idea of the absolute amount of colloidal matter present.

there is a close similarity between the behaviour of many clays and that of a fine concrete composed of Portland cement and fine sand, the freshly-made concrete possessing a considerable amount of plasticity even when the total proportion of colloidal matter present is extremely small. A careful comparison of the structure and properties of such a concrete with those of a plastic clay gives a very clear idea of the possible nature of clay and especially of that of its most characteristic property—plasticity.

The properties of clays which are most closely allied to those of colloids or mixtures of colloids and inert materials differ according as the clays are respectively in the dry, pasty, or " slip " state. The pasty condition is produced by reducing the clay to a powder by grinding, and then mixing it mechanically with a suitable proportion of water. Some highly plastic clays occur naturally in the form of a stiff paste which may be softened by crushing between rolls so as to reduce to thin sheets and mixing this mechanically with water. Clay is converted into a slip or slurry by grinding or crushing it and then mixing with a sufficient quantity of water to keep the clay in suspension. The amount of clay which can be suspended in a given volume of water depends on the physical condition of the clay and the presence or absence of very small amounts of alkali, acids, or salts in the water.

The following properties of clay can be most satisfactorily explained by assuming the presence of colloidal matter :—

*Water is absorbed* by any clay in fairly definite proportions which appear to have some relation to its plasticity, the lean clays absorbing much less water than the more plastic ones.

When clay is completely dried without being excessively heated, it is highly hygroscopic and absorbs water readily—sometimes up to 15 per cent. of its weight—without becoming appreciably moist. It is, therefore, difficult to keep clay perfectly dry, and most specimens contain a considerable proportion of water which may, in some cases, cause the clay to be tough and plastic.

The hygroscopic nature of clay distinguishes it from silt and sand. When a piece of air-dried clay is placed in water, the latter enters into the pores, drives out the air, and lifts up the smallest particles of clay, disturbing the structure of the material so that a partial or complete breakdown or slaking occurs. The disruptive action of the water on the solid particles forming the clay mass may be attributed to a molecular attraction between the water and the clay whereby the water wets the surface of the latter and the resulting interposed film of water reduces the cohesion of the clay grains so that they separate easily. The absorption of water is accompanied by a slight rise in temperature, which though scarcely noticeable is characteristic. The amount of water absorbed varies greatly with different clays; in some cases, it is equal to 80 per cent. of the weight of the clay.

Rohland[5] suggests that this power of imbibing a definite amount of water is due to the colloids in the clay, and that as soon as the clay has absorbed a sufficient amount of water to convert its colloids into the form of a colloidal sol its ability to absorb water reaches a saturation point and ceases; this is proportional to the colloids

present, and probably, roughly to the plasticity of the clay. It may, however, be proportional to the capillary spaces between the clay particles.

In the manufacture of articles from clay paste, it will be found that each kind of clay requires a definite proportion of water for its efficient manipulation. If more is added it will become too weak, if less it will become too short. This water is known as "water of formation," and its amount has a theoretical as well as a practical importance, being closely related to plasticity. Unfortunately, there is no certain method of ascertaining the consistency of the clay paste, nor of ascertaining when the correct proportion of water has been added to a clay. The ordinary method consists in adding such a proportion of water that when the mixture is worked up into a paste it readily receives the impression of finger-prints, but does not adhere to the skin, the amount of water required being found by trial. This procedure is too rough for scientific purposes.

If water is added to a moderately plastic, dry clay in increasing quantities, the clay can at first be moulded with difficulty, then more easily, and later it may be moulded with the greatest facility. If the proportion of water is still further increased, the clay becomes sticky, then fluid, and it is eventually impossible to form it into any definite shape.

If the same experiment is repeated with a more plastic clay, using the same proportions of clay and water as before, it will be observed that it will adhere to the fingers and will allow of no further shaping unless its plasticity is diminished by adding non-plastic material or altering the proportions of clay and water.

An excessively lean clay, on the contrary, only acquires the desired plasticity when it has a very soft consistency, which does not allow it to remain in any given form, and it must, therefore, be rendered more plastic if it is desired that it should be shaped by hand. If the formation is done by mechanical means, in which the clay is subjected to much stronger pressure, less water must be added to the body in order to give it the required plasticity, and it will be expedient to make it of a stiffer consistency. Pressure, in this case, plays the same part as water in the plastic qualities of clays; the one can be partially replaced by the other, so that if the amount of pressure is increased the proportion of water should be diminished and *vice versâ*.

If a sufficient quantity of water is added to a clay to form a slip or slurry, the latter will have certain characteristics, according to the proportion of water and clay, to the nature of the clay and the purity of the water. If the proportion of water is very large and the particles of clay difficult to separate, they may fall to the bottom very soon after the mixing ceases, or the greater part of them may so fall, leaving only the smallest particles suspended in the water for many hours. With high grade clays, such slips have marked colloidal properties (see *Viscosity, Adsorption, &c.*).

Slips containing about an equal weight of water and clay are largely used in various branches of clay-working, for covering other clays of inferior quality when burned, and for making objects by the

process of casting. In the former case, the articles to be covered are immersed in the slip, and in the latter, the slip is poured into plaster moulds and allowed to remain for a short time, after which any superfluous slip is poured away. On allowing the mould to dry, the water is absorbed by the plaster, and the clay article may be removed in due course.

In both cases, it is necessary that the proportions of clay and water should be carefully adjusted, in order to obtain the best results. When a suitable mixture has been obtained, it will usually be sufficient to weigh exactly one pint of it accurately, and to dilute other mixings with a stronger slip or with water, until they reach the same weight per pint. The specific gravity of the slip may be determined with great exactness in a pycnometer, if desired, but this involves unnecessary trouble for most purposes.

Schwerin has found that water and alkalies in the clay slip may be removed by electro-osmosis by connecting the bottom of the tank containing the slip with the negative pole and the cover with the positive pole of a battery when, on passing a suitable electric current, the water and alkali will collect at the bottom, and the slip will become very stiff and apparently—though not actually—dry.

The *hygroscopicity* of dried clay is very marked, up to 20 per cent. of water being absorbed from a damp atmosphere by some clays. It does not necessarily prove the presence of colloidal gels, but if they were present such hygroscopicity would be anticipated.

*Miscibility.*—It is a remarkable fact that highly plastic clays, in addition to having a limited power of absorbing water, are incapable of forming a uniform mixture with less plastic clays. According to Rohland[5], this is due to the fact that when colloids in clay are coagulated they form gels which cannot be brought into solution by the addition of more water, and resist the absorption of water. They are also incapable of taking up anything from a second colloid. Hence, if the colloids are coagulated, as in very plastic clays, they will not absorb more than a certain amount of water, will not take up other plastic clays, and will not mix homogeneously with them. Many objectionable qualities of a highly plastic clay may be obviated by saturating it with water and then adding a suitable amount of non-plastic material. In this way, also, highly plastic clays gain the power to be mixed thoroughly with other plastic clays and with felspar, which forms coagulable colloid solutions.

Rohland has found that plastic clays in which there is only a small proportion of colloids, and these not coagulated, may be uniformly mixed with other similar clays.

*Deflocculation.*—Clays usually exist in large masses which are not readily affected by water, but smaller pieces may be broken down or "slaked," as just described, in a manner which is very similar to the deflocculation of colloidal gels. If a suitable electrolyte such as sodium hydroxide, carbonate or silicate, or baryta is added, the amount of suspended matter is increased, as with well-known colloids, and, if an acid is added to the suspension, the clay particles are rapidly precipitated like a coagulable gel. Clays are remarkably

sensitive to the action of electrolytes, a very small quantity of a solution of soda being capable of converting a clay-paste into a viscous fluid which, on the addition of just sufficient acid to neutralise the alkali, will again become solid. This behaviour bears a remarkably close resemblance to the action of electrolytes on the coagulation and deflocculation of colloids. Rohland[5] has suggested that the formation of a clay slip (sol) may be explained as due to the action of electrolytes on the colloids present in the "clay." With a negative sol in colloidal suspension, the most powerful factor in coagulation is the positive ion of the electrolyte added, the negative ion having but little influence. The power of different positive ions appears to be the same for those of the same valency, but divalent and trivalent ions are more powerful than monovalent ones. Thus, Foerster has shown that if a clay contains just enough calcium ions to keep the colloidal matter in the gel state, and sodium carbonate is added, the sodium will combine with the colloid clay so as to form the sol, the plasticity being reduced according to the completeness of the reaction, but if an excess of sodium ions is added they will recoagulate the colloid. This has been confirmed by experiments on the viscosity of clay slips by Mellor and others.

The addition of electrolytes to a clay body also affects some of the materials present. Thus, Schurecht[8] has found that the working properties of mixtures of graphite with sufficient plastic clay to act as a binder, such as are used in the manufacture of plumbago crucibles, are considerably improved by the addition of 0·3–0·4 per cent. of sodium hydroxide or, in some cases, of hydrochloric acid, according to the nature of the colloidal matter present.

Kosmann[9] attributes the disintegration action of alkaline solutions on clays to the solution of a siliceous film on the particles which acts as a binder. This explanation scarcely seems to account for the great effect produced by so small a proportion of soda.

When clay is saturated with water and an electrolyte is then added, the adhesion of the particles is reduced, partly as a result of the osmotic pressure of the solution on the porous particles[10] which then act as a permeable diaphragm and force the water more strongly into the interior of the particles than would be the case if plain water were used. If the basicity or alkalinity of the solution is altered by the addition of an acid, the particles tend to coagulate and adhere to each other with the result that the mass becomes semi-solid.

When clay is suspended in a liquid having a higher coefficient of capillarity than water (*e.g.*, acids) the particles tend to precipitate, but in a liquid with a lower coefficient than water (*e.g.*, bases and alkalies), they tend to remain in suspension. This behaviour is attributed to the difference in the adhesion of the fluid particles of the liquid to the particles, the surface of the smallest particles being much greater in proportion to their weight than that of the larger ones.

Adolph Mayer has determined the limiting power of electrolytes which permit a fine clay (freed from carbonates and soluble salts by treatment with hydrochloric acid) still to be kept in suspension in water (100 grammes clay, 500 grammes water). The limits are :— ammonia, 2·5 per cent.; sulphuric, hydrochloric, and nitric acids

and the alkali salts of these acids, 0·025 per cent. Although 2·5 per cent. of ammonia caused precipitation in Mayer's experiments, a less amount favours deflocculation, or breaking up of the lump.

The "*fluidity*" of any clay slip depends chiefly on the proportion of water added, but it is largely affected by the presence or absence of very small proportions of electrolytes. According to Rohland[5], the addition of hydrochloric, nitric, sulphuric, acetic, or propionic acid increases the plasticity of the clay slip, apparently by coagulating the colloidal matter present. Solutions with an acid reaction such as sal-ammoniac, aluminium chloride, ferric chloride, and potassium bichromate behave similarly. Alkalies such as ammonia, caustic soda, caustic potash, lime-water, baryta, and basic salts, make the slip more fluid and reduce the plasticity of the material, but their behaviour depends on their concentration. The action of alkalies in reducing the viscosity, sometimes requires several days, and is accompanied by coagulation. An excess of alkali may cause a reversion of this action, the viscosity increasing again. The addition of salts usually decreases the osmotic pressure and increases the viscosity.

Acheson has patented the use of a solution of tannin and alkali to make a clay "fluid," and, followed by the addition of an acid—presumably by precipitating the colloid matter—to increase the plasticity of the clay.

The *viscosity* of clay suspensions, before and after the addition of various substances, can best be understood by assuming that it varies according to the condition, and proportion of the colloidal matter present. Mellor, Green, and Baugh[11] have arranged the substances likely to be present in, or added to, clays into five groups according to their action on the viscosity of the clay* :—

(1) Substances which first make the slip more fluid, while further additions stiffen the slip. Examples: sodium and potassium carbonates, fusion mixture, potassium sulphate, potassium bisulphate, potassium hydroxide, potassium nitrate, sodium sulphide, tannin and gallic acid.

(2) Small amounts thicken the slip; larger amounts make the slip more fluid. Examples: copper sulphate, dilute ammonia, and potassium aluminium sulphate.

(3) Substances which make the slip thinner: magnesium, mercury and sodium sulphates, sodium sulphite, sodium acetate, sodium chloride, sodium phosphate, ammonium gallate, hydrochloric acid, water-glass. It is just possible that some of these substances may have to be transferred to the first (or second group) if greater (or less) concentrations be tried than those employed by Mellor, Green, and Baugh.

(4) Substances which only stiffen the slip: grape sugar, humic acid, ammonium chloride, calcium chloride, calcium

* It should be noted that the slips used were not made from a single clay, but from a body mixture consisting of 16g. ball clay, 19g. China clay, 13g. Cornish stone, 20g. flint and 100 c.c. water. To this mixture, varying quantities of acid, alkali and salt—ranging from 0·1 to 6g. or 0·1 to 35 c.c.—were added. This may account for the difference between these results and those obtained by some Continental investigators.

sulphate, ammonium urate, aniline, ethylamine, methylamine. Here, again, some of these substances may have to be transferred to the second (or first) group if greater (or less) amounts than those mentioned are used.

(5) Substances which have no appreciable effect on the slip : *e.g.*, alcohol.

Rieke has stated that the most soluble substances increase the viscosity of the slip, but their effect may be neutralised by the addition of a solution of barium hydroxide. The most harmful sulphates according to the same investigator are those of calcium, aluminium, and the heavy metals. Alkali sulphates stiffen the slip when only 0·1 per cent. is present; larger proportions render it thinner until 1 per cent. is reached, after which they stiffen it again. Zinc and copper sulphates exhibit this phenomenon of variableness to a marked degree.

Bleininger found that the first addition of clay (up to 3 per cent.) decreased the viscosity of water on account of the deflocculation of the clay by dilution and the solution of the contained electrolytes. When, however, the addition of clay became so great that no further matter went into solution and the effect of the gel showed itself, the viscosity increased with each addition of clay. This negative viscosity is peculiarly characteristic of some clays.

The *size of the particles* of the purer clays is comparable with that of colloidal particles, but most clays contain so large a proportion of larger particles that it is almost impossible to isolate those which are colloidal, in an entirely satisfactory manner.

The *adsorptive power* of clays bears a striking similarity to that of colloids, or rather to that of a mass of inert material, the particles of which are covered with a film of colloidal matter which also fills some of the interstices. Thus, clays adsorb soluble dyestuffs, tannin, humus, oil, grease, salts,* &c.; and Hirsch and others have found that barium, lead, and aluminium salts are adsorbed more readily than those of lime and magnesia. Chlorides and nitrates are adsorbed more than sulphates, but alkali salts with the exception of the alkaline carbonates are not adsorbed. The behaviour of the alkaline carbonates may be explained by the almost invariable presence of calcium ions in clays, which react with the carbonate forming a precipitate of calcium carbonate, and so removing the carbonate ion from solution. Rohland[5] states that some clays which are only moderately plastic may, on the addition of alkali and certain salts, or through some chemical change, be made more adsorptive. The adsorptive power of clay is valuable in some industries, and it is on account of this power that if clay is mixed with neutral or slightly acid muddy solutions or emulsions, when the clay settles it will be found to leave a clear liquid. The adsorption of a clay is usually determined by noting the loss of colour of a dye solution such as malachite green, and comparing it with another similar solution to which a standard clay has been added.

* Many clays retain salts so tenaciously that it is impossible to wash them clean with plain water, but they can be removed by washing with a solution of a salt which is more readily absorbed by the clay.

If Olschewsky's suggestion that the particles of clay are porous is correct, the phenomena ascribed to adsorption may really be due to adsorption within the capillaries or pores.

The " scum " observable on some bricks is due to the salts adsorbed by the clay and carried to the surface during the drying of the bricks.

The *capillary phenomena* shown by many clays and soils may also be explained on the hypothesis that clays are colloidal in character.

The *porosity* of clays varies with the amount of water present, some stiff plastic pastes being quite impervious, though the same materials are porous when dry. This porosity appears to be associated with the capillary structure of many clays and whilst it is a property possessed by non-colloidal substances, it is a characteristic property of some colloids.

The *semi-permeability* of clays, like that of colloids, is a characteristic property, and although its nature is by no means well understood, it appears to confirm the presence of colloidal matter in clays.

When clays are made into semi-permeable " membranes," they behave according to their plasticity. The plastic clays effect a perfect separation between the colloid and crystalloid solutions and are truly semi-permeable, but very lean clays such as china clay are very irregular in their action. In some cases, the presence of a crystalloid may cause a sol to pass through a membrane, as when silicic acid is mixed with sodium chloride both will pass through. It is also stated by W. Ostwald[12] that fresh colloids (particularly silica) will pass through a membrane, but after keeping a few days they will not pass through. There is no connection between the rate of diffusion through the membrane and the molecular weight.

According to Rohland[5], plastic clays will allow ferric chloride and sugar (crystalloids) to diffuse, but not tannin (colloid). In emulsions of oil and water, plastic clays permit the (crystalloid) water to pass, but not the (colloid) oil. In alcoholic solutions of fat, such clays permit the alcohol to pass but not the fat. In aqueous rubber solutions, plastic clays prevent the rubber from diffusing, and in albumen, solutions the albumen is retained, both rubber and albumen being typical colloids. The diffusibility or speed at which the substances dialyse through the membrane depends upon their nature. Thus, water* which is a crystalloid, and electrolytes, *e.g.*, salts dissolved in it, diffuse rapidly, but colloids, such as ferric hydrate, hydrated silica, hydrated alumina, and most products of organic life such as starch, vegetable oils, and gelatin are either indiffusible or pass through with extreme slowness. Colours, on account of their complex composition, play a special part; they are retained by plastic clays, though these colours are crystalloid and not colloid. Berlin blue, potassium ferricyanide, aniline blue, sulphated triphenyl rosaniline, aniline red, carmine, malachite green, fluorescin, aurin, and other animal, vegetable, and tar colours, cannot diffuse through clay, and this, in spite of their crystalloid nature.

* Zschokke[14] suggests that plasticity is possessed by all substances composed of extremely minute particles with sufficient affinity for each other and with a power for combining with water.

The explanation of semi-permeable membranes most widely accepted at the present time is that of selective solubility, suggested by L'Hermite[13]. The membrane is permeable to those substances which dissolve in it but not to others.

As the semi-permeability of clays appears to be connected with the plasticity, any treatment which will increase the latter should increase the former. Rohland[5] has found this to be the case with some lean clays he has examined. Some of the phenomena occur whenever plastic clay is mixed with solutions, as the particles allow the crystalloids in the latter to pass through them, but retain the colloids on their surface. In this way, the adsorption of crystallised matter as well as colloidal matter occurs; but as the particles of clay are so minute the effects are scarcely distinguishable, and clays appear to be capable of absorbing both colloidal and crystalloidal substances.

The *permeability* of raw clays has been studied by Spring, who found that when such clays are confined so that they cannot expand, they will only absorb enough water to fill the pores. The amount absorbed varies from 3 per cent. with some fireclays to 25 per cent. with some sandy loams. When not confined in this manner, the extent to which the water can permeate a clay is dependent on the amount of non-plastic material it contains, and increases when sand or grog is added. The permeability of a fired clay is an important characteristic, and is described later.

The more permeable a clay, the more easily can it be dried and heated without damage, large pores being prefereable to small ones.

Wet clay in the form of a stiff-plastic paste is generally considered to be extremely impermeable, but, as already mentioned, this is only a relative property, as such a mass of clay, if left in water, will, in time, fall to pieces. Clay which has been suspended in water and allowed to settle is usually quite permeable, as are many natural clay deposits. It is only when the material has been " worked " or " pugged " that it becomes impermeable.

The *plasticity*[1] of clays is one of their most important properties. Plasticity may be defined as that property of a material which enables it to change its form without rupture, the new shape being retained when the deformatory force is removed. In other words, a material is said to be plastic when it can be kneaded or pressed into any desired shape, and remains in that shape when the kneading ceases or the pressure is removed; this alteration of shape being capable of being repeated indefinitely. It is a characteristic of many substances besides clays,* though clays possess it to the most marked degree. Ashley[7] has pointed out that very few people agree exactly with the conception of plasticity. Thus, a brickmaker terms a clay plastic when it works well in his machine, and is capable of being kneaded into a " good " paste, but a potter usually places more emphasis on the binding power of the clay, though he terms this its plasticity.

Although these definitions are sufficient for practical purposes, they are not entirely satisfactory, nor is there any explanation of the

* The " possible plasticity " is that which can be developed under the best known conditions. For many purposes, it is not necessary to develop the plasticity of a clay to the utmost.

causes of plasticity which meets all the needs of the case. Plasticity varies with different samples and on different occasions, though no raw moist clays are entirely devoid of plasticity. Clays which are quite dry are not plastic, but become so when mixed with a suitable proportion of water so as to form a paste. Hence, the amount of plasticity developed is dependent on the proportion of water present.

Liquids other than water may be added to the clay to produce plasticity, but they must usually contain water, and even then, sometimes produce quite different characteristics. Thus, glycerine may be used, but it prevents the clay from drying, and Krupsay has pointed out that if plastic masses made from clay and glycerine and clay and water respectively be kneaded together the resulting mixture is non-plastic. Fatty liquids, such as oils, seem to make a more plastic body than with water, especially if the clay has been dried so as to take away from it the hygroscopic water, but alcohol, ether, and turpentine produce bodies with little or no plasticity.

The nature of the plastic product formed when liquids other than water are used is worth further study. In the case of an oil, the plastic mass is quite different from that produced with a liquid such as anhydrous nitric acid, anhydrous sulphuric acid, absolute alcohol and glycerine. Each of these fluids is soluble in water, and is, therefore, able to wet the hydrated clay grain with its attached water molecule and to separate the grains sufficiently to produce a plastic mass. In each case, the clay may be "dried" again and made plastic with any of the other fluids. According to R. F. MacMichael[15] only those liquids which "wet" the clay particles can produce plasticity. Water and fatty oils do this, but ether, gasoline, kerosene, engine oil, and similar fluids which do not "wet" the clay grains are either unable to penetrate between them and so do not develop plasticity in the clay or they form a film of such a nature around the clay grain as to prevent cohesion, so that the mass acts like sand and water, but there is no gradation or balancing of the forces, as is necessary in order to obtain true plasticity.

Plasticity also depends both on the nature of the fluid and that of the solid. Thus, while both water and oil wet quartz sand, water under suitable conditions will easily displace oil films from a mixture of sand and oil. On the other hand, both oil and water wet zinc oxide, but in this case the oil will readily displace the water films, forming paint or putty. The resulting mass, in this case, may be said to be oleated, in very much the same manner as clay is said to be hydrated. The same principle is employed commercially on a very large scale in the flotation of metal-bearing ores.

The possible plasticity[2] of clay or other substance cannot be developed by commercial methods of grinding unless the material is in a state which may be regarded as dormant plasticity. This has been regarded as an objection to the view that plasticity is due to the colloidal properties of clay, but the objection may be met by the difficulty of reducing some clays to so fine a state as is required to produce the requisite amount of colloidal matter.

Plasticity also varies with the presence of certain other substances; thus, the following soluble substances reduce the plasticity of clay:

ammonia, caustic soda, caustic potash, lime, sodium carbonate, potassium carbonate, borax, and water glass. They appear to do this by coagulating the colloidal portion of the clay, but their action may be prevented by the addition of a sufficient quantity of weak acid to neutralise the alkali in the clay.

The addition of certain organic acids as humus, or of gum, glue and starch confers a pseudo-plasticity on clay which is, however, quite different from true plasticity and makes the clay "sticky" rather than plastic.

The *stickiness* of certain clays (*e.g.*, London clay) is very pronounced, but must not be confused with true plasticity. Ashley[7] has stated that if the granular constituent is removed from a plastic body it loses plasticity and becomes sticky until the granular constituent is restored. This suggests that the practice of adding granular material of a non-plastic nature, so common among the users of London clay is based upon a sound principle. The stickiness of clay may be regarded as due to colloidal material which is not properly distributed throughout the inert granular mass.

Plasticity does not appear to be connected with the chemical composition, as clays which yield the same results on analysis may differ widely in plasticity, yet on heating above 415°–600° C. all clays lose their plasticity, and it cannot be restored. It is also a curious fact that the clays which are richest in "true clay" are seldom so plastic as those which are not so pure, so that any peculiar structure of the clay molecule can scarcely account for its plasticity, though several eminent investigators have laid stress on this suggested cause.

Several investigators have attributed the plasticity to the shape or size of the clay particles. Thus, Aron considered plasticity was due to the particles being spherical, but Zschokke, Biedermann, and Herzfeld dispute this, and attribute it to the presence of flat and laminated crystals,* a view early put forward by Johnson and Blake, and held later by Bourry[16], who stated that plasticity becomes greater in proportion as the grains diminish, and that all minerals if reduced to a sufficiently impalpable powder, will on the addition of a liquid produce bodies having a certain amount of plasticity.

According to Le Chatelier, the lamellar structure and the well-known capillary attraction are a sufficient cause of plasticity. He has shown that all plastic masses contain a large proportion of air by comparing their density with that of clay and water, and that in each plastic mass there are innumerable capillaries of not more than one three-thousandth of an inch in diameter. He concludes that the tension of the menisci between the water-surface and the air-surface in these capillaries explains the toughness of the plastic mass, as the capillary force prevents the mass from breaking up under pressure, but allows the minute particles to slip over each other, and yet adhere so strongly that the mass retains the new form when the pressure is removed. In other words, clay is plastic when sufficient water is

* The particles are so extremely minute that it is exceedingly difficult to ascertain their shape. Le Chatelier has noticed that if the material is disturbed when under the microscope, the crystalline form may be observed for a fraction of a second by polarised light if their symmetrical axis is perpendicular to the microscope axis. As soon as they are flat they are isotropic.

added to induce the cohesion to a point where it can readily be overcome by the pressure of the worker's hands, *i.e.*, to 1–3 lb. per square inch, so that it is a balancing of forces producing a peculiar combination of fluidity and rigidity in the mass of wet clay; under a light pressure it acts as a rigid body, under a heavier pressure, it acts as an imperfect fluid. The rigidity is attributed to friction between the clay grains, so that a mass of clay retains its form until acted on by a force sufficient to overcome this friction and produce distortion. The fluidity of the wet clay is due to the freedom of the individual particles to move over each other, after cohesion has been partially neutralised by the addition of water.

The theory that plasticity, instead of being a special property, is simply the result of molecular attraction, and that all bodies which are made up of laminated particles must become plastic when they are reduced to sufficiently impalpable powder has been confirmed by Vogt as regards mica, which is highly laminated, being made up of thin layers, and when reduced to an impalpable powder becomes distinctly plastic if water is added. The insistence laid by Bourry[16] on the laminated structure of the particles has been frequently overlooked, and the suggestion that, because burned clay may be ground equally fine and yet never become plastic his experiments are not conclusive, is irrelevent.

Seger[1], and independently Schumacher, consider plasticity to be due to molecular differences in the clay particles, and Bischof agrees with the latter in considering that clay has undergone great changes in density during deposition, and a kind of " felting " of the particles has resulted so that they adhere much more closely to each other than the quartz and other particles in which this felting process has not taken place.

Wolff has calculated the attraction of the particles of various substances to each other on the assumption that they are spherical. He finds that the mutual attraction of the clay particles is very high and that the ratio between their mutual attraction for each other and for water is much higher than for any other substances examined. He stated in confirmation of this theory that other substances can be made plastic, if they can be made sufficiently small, as by precipitation.* He also pointed out that the combined water in a clay particle increases the ratio considerably and is accompanied by an increase in plasticity not only in the clay, but in alumina and iron oxides. Zschokke confirmed this theory, and has shown that clay particles have a thicker film of water around them than particles of non-plastic materials such as sand.

It is extremely difficult to find satisfactory reasons for attributing the plasticity solely to the plate-like or lamellar structure of the particles or to purely mechanical or chemical characteristics in the atoms and molecules of the clay and water, though these are undoubtedly important. Nor has the effort of Le Chatelier to find the source of plasticity in the presence of small amounts of impurities proved really helpful. The smallness and shape of the particles appear to be important, as clay ground in a pan-mill is more plastic than when a ball-mill is used, as the former flattens out the material,

but this does not really affect the cause of plasticity. Grinding is not a cause of plasticity, though Johnson and Blake claim to have made a non-plastic china clay plastic by fine grinding.

It has been suggested by Olschewsky, who based his experiments on those of Daubée, that the water used has a chemical action, and that plasticity is due to the formation of a system of capillaries in the clay, a felt-like or spongy material being formed, and in this way, the clay particles are able to come into closer contact, owing to the production of a kind of gelatinous or colloidal film, but the presence of an alkali appears to be essential for this alteration to take place. Thus, Mellor found ground pottery, felspar, and Cornish stone become plastic on heating with water under pressure to a temperature of 300° C. for several days, but china clay and flint are scarcely affected. The finer a substance is ground the more complete is its reaction with water, because a small particle has a greater surface in proportion to the water than a coarse one. If the particles are sufficiently fine, water may, indeed, act in a similar manner to a caustic alkali; thus, very finely divided silica becomes colloidal when brought into contact with boiling water, just as coarser particles do when brought into contact with a boiling solution of caustic potash.

Koerner found that other substances (as alumina) become sufficiently finely divided in water, but their power of cohesion is lost on drying, and suggested that the plasticity may be brought about in a similar manner. This would explain why it is impossible to produce highly plastic clays from kaolin.

As many organic substances possess certain characteristics of plasticity, several suggestions have been made that these may be the cause of plasticity in clay. It is found, however, that there is no definite relation between the plasticity and the proportion of carbon in the clay, dark coloured clays, rich in carbonaceous matter, being no more plastic than lighter ones almost free from this material.

Several observers have suggested that bacteria produce plasticity, but Hecht and Gosmann have not found sufficient data to warrant this suggestion, especially as it has not been found possible to increase the plasticity of clay by inoculation.

Whenever plastic clay is subjected to pressure it tends to obey the laws of fluids, transmitting its pressure to all parts of its mass and flowing through an orifice through which it can escape, though it is far from being a perfect fluid. From this arises the modern conception of clay as a very viscous liquid in which every particle of solid matter is surrounded by a film of liquid, so that the particles are virtually in a state of suspension, and hence, that a plastic clay is, at any rate in part, in a colloidal condition.

As far back as 1872 Schloesing* suggested that the plasticity of clay was due to its colloidal nature, and claimed to have found an amorphous material of the same composition as kaolin which had all the characteristics of a colloid, and was termed by him *argile colloïdale*. Very little notice was taken of this suggestion or of the

* This has more recently been confirmed by Cohn and Atterburg, who found that precipitated barium sulphate and calcium fluoride are both plastic when fresh.

allied work of other observers until 1896, when Rohland[6] investigated the subject further, and found indications that the colloidal nature of clay appeared likely to explain many of the facts noted in regard to plasticity.

The nature of the colloid material apparently existing in many clays has already been described. In attempting to explain plasticity as being due to these colloids, it is assumed that some or all of the pores of the clay are filled with a colloidal solution (gel) obtained by the partial hydrolysis of the clay, and that the larger the proportion of pores so filled, the fatter and more plastic will be the clay, provided the proper ratio of granular material to colloid gel is retained.

Rohland[5] and others have further shown that the addition of trifling amounts of electrolytes often produces great changes in the plasticity of a clay, and suggest that this characteristic of colloids is a strong argument in favour of the connection between the colloidal material in clay and plasticity. All electrolytes (such as acids) which yield hydrogen-ions on dissociation, increase the plasticity of clay, whilst those (such as alkalies) which yield hydroxyl-ions make a clay more fluid.

Plasticity is not, however, entirely due to the presence of colloidal matter in clays, though the effect of colloids in increasing plasticity cannot be denied. Hermann and others maintain that the presence of inorganic colloids in clay has never been conclusively proved. It should be noted that clay may be suspended in water and then precipitated or deflocculated indefinitely without impairing its plasticity. This is not usually the case with true mineral colloids, which usually set irreversibly and do not return to the colloidal condition. Moreover, the whole of any individual clay grain is not softened upon the addition of water. Repeated wetting and pugging does not materially alter the size of the grains or change their general outline or appearance. This would not be the case if the clay were softened and reduced to a homogeneous mass, wetted, and subsequently broken up with the formation of new grains when it was dried and ground. Whether wet or dry, under the microscope, the grains retain the appearance of a sharply-defined body.

Another difficulty has been pointed out by J. M. van Bemmelen, viz., the rapidity with which colloids lose their power of absorbing water. This suggests that clays of great geological age cannot contain active colloids produced when the clay was formed, though they may contain colloidal substances derived from adventitious materials—organic or otherwise—at a comparatively recent period. The fact that many highly plastic clays appear to be free from such extraneous colloids only increases the difficulty regarding the latter as the cause of plasticity. Other objections of equal or greater weight may be urged against any single theory yet published on the causes of plasticity so that much further work requires to be done.

Summarising the results of the numerous theories and experiments made, plasticity may be said to be due not to one, but to several causes, the chief of which are :—

(i) The nature of the molecules of " true clay " present.

(ii) The extremely small size of the particles, their lamellar shape, large surface (due to their porosity), and (possibly) their fissile character. In such small particles, the phenomena of cohesion are quite different from those in larger particles.

(iii) The hydrolysing action of water on the particles and the probable production of inorganic colloid matter. If this is absent or neutralized by hydrogen-ions added purposely or occurring naturally or through fermentation of the organic matter in the clay, the plasticity will continue to increase until an excess of hydroxyl-ions is again produced; when the concentrations of hydroxyl-ions is large, the negatively charged clay particles will go into suspension. As the extent to which water can be dissociated is very limited, the plasticity of the clay can only be increased at so slow a rate that it is unlikely that slightly plastic clays (kaolin) can ever be made highly plastic by artificial means, though the increase in plasticity may be sufficient to show the nature of the reactions which take place.

(iv) The presence of organic colloid matter due to impurities in the clay, or added purposely, may still further increase the plasticity.

(v) The presence of minute quantities of soluble salts may exercise a pronounced effect on the plasticity. Their action has been mentioned under *Viscosity* (p. 121). Plasticity appears to be a resultant of several properties (see also *Cohesion, Adsorption, Tensile Strength, Binding Power*, &c.).

*To increase plasticity.*—The limits within which the plasticity of clay may be increased by the addition of soluble salts are very small, but there is such an abundance of naturally plastic clays that it is only where materials of exceptional purity are required that an increase in plasticity is desirable.

A small increase in plasticity may be obtained :—

(1) By increasing the hydrogen-ions in the material, by allowing the organic matter in the clay to decompose (ferment) and become acid, by adding weak acid, or by keeping the clay in intimate contact with fresh water by stirring the two together. This appears to hydrolyse the clay and forms colloid matter on the particles. It is important to have the particles of clay as small as possible in order to facilitate the hydrolysis. If water alone is used for this purpose, the clay must be allowed to stand until fermentation of the organic matter begins, and the mass reacts faintly acid. In any case, the time required for an appreciable increase in the plasticity may be several years. No addition of any electrolytes or substance other than plastic clay can increase the true plasticity of a paste chiefly composed of non-plastic materials. Many of the so-called " lean clays " are of this nature; they are rich in inert matter, but the proportion of colloidal matter in them is very small. Such clays can only be made more plastic by removing a large proportion of the inert matter naturally present in them or by

the addition of a highly plastic clay. The addition of electrolytes to such clays is only of value when their low plasticity is due to the clay gel present having become hardened or coagulated, but is still capable of being revived or deflocculated by means of an electrolytes or other simple treatment.

(2) By keeping the clay in a moist damp cellar. This is termed "ageing" or "souring."

(3) By the addition of colloids such as colloidal silica, alumina, or iron hydrate, hot starch, dextrin, tannin, rubber, sumach, inulin, caramel, gelatin, gum, glycogen, or various ferments and enzymes, the plasticity of the clay may be increased, but care must be taken to avoid confusion between true polasticity and the pseudo-plasticity caused by the addition of materials of an oily, gelatinous, or gummy nature.

Some very interesting experiments by Acheson and Ries on the effect of a 2 per cent. solution of tannin (gallotannic acid) on clay show that the addition of this substance notably increases the plasticity of clay, and at the same time apparently deflocculates it and breaks it up into finer particles. The tensile strength of the clay was nearly doubled.

In a later patent, Acheson first adds tannin and alkalies or ammonia and stirs the clay into a fluid state, and then by the addition of a suitable quantity of acid he coagulates the colloids and forms a stiff paste.

(4) By reducing a sufficient number of particles to so minute a state that they assume colloidal properties in the presence of water. Thus, by very prolonged grinding with water many hard clays[1] become appreciably more plastic.

The softer materials become exceedingly smooth and plastic; the harder ones yield less readily to the treatment, but still develop marked pasticity, very similar to that of normal clay heavily overloaded with sand or grog.

By selecting the materials and method of grinding, many degrees of plasticity may be obtained, from that of a very smooth plastic clay to that of a very short sandy clay, indicating that the difference is one of degree and not of kind, the essential characteristics being that the clay or other materials shall occur in a state of very fine subdivision, and that their surfaces are readily wetted by water. The chief practical difficulty lies in grinding sufficiently fine, as the smallest particle that can be seen under the microscope does not by any means represent the limit towards which the grinding should proceed. The plasticity produced by artificial grinding depends on the size and shape of the particles, and only indirectly on the material of which the plastic mass is formed.

*To reduce plasticity.*—(1) Hydroxyl-ions may be added and the temperature raised (direct reduction). (2) Non-plastic material may be added so as to spread the plasticity over a larger volume of material

[1] Plastic material has been formed in this way from slate, plaster moulds, iron ore, ashes, lava, limestone, sandstone, burned brick, silica, mica, felspar, and even glass.

(indirect reduction or dilution). (3) The material may be heated to 200° C. or other suitable temperature.

For the first method, any basic material, either organic or inorganic, may be used though lime water is the cheapest. If lime is too weak in hydroxyl-ions, caustic soda may be used, as may any salt composed of a strong base and a weak acid, such as sodium (or potassium) phosphates or silicates, all of which readily hydrolyse and yield hydroxyl-ions, though the cation constituent of the salt may exercise a considerable effect. Thus, borax reduces the influence of the hydroxyl-ions and potassium carbonate increases it, yet both are salts composed of a strong base and a weak acid. The concentration of the alkaline or basic material added is also of importance, and it may be necessary to render sulphates and other soluble salts insoluble by the addition of baryta, as suggested by Weber. Certain clays, as Weber has shown, act in precisely the reverse manner. These are free from sulphates, and appear to be rich in colloidal matter.

Certain clays containing organic acids of a fatty nature are saponified on treatment with alkali, and the soap so produced increases, instead of diminishing, the plasticity, owing to the coagulation effected.

The reduction of plasticity by raising the temperature considerably is described later. A comparatively small rise in temperature produced by the action of mechanical stirrers—will reduce the plasticity of clay if free hydroxyl-ions are present.

The addition of non-plastic material, such as sand or grog, effects a reduction of the plasticity in an entirely different manner, by separating the clay particles from each other. It thus reduces the strength of the material, but by diminishing the shrinkage, it enables the clay to be used in a manner which would, otherwise, have been impossible, and the strength is seldom reduced sufficiently to make any notable difference to the user of the material. The proportion of non-plastic material to be added depends on the size of its grains and on the binding power of the clay. As the latter is closely connected with its plasticity, it will usually be found that the more plastic the clay, the larger the proportion of non-plastic material which may be used.

Some sands are quite useless for this purpose, so that great care is needed in their selection. For some clays, chalk, flints, or grog is preferable to sand.

The *measurement of plasticity* is a problem which has not yet been satisfactorily solved, probably for the reason that plasticity is the result of the united action of several forces some of which may not, as yet, have been recognised as important. Early attempts to measure plasticity usually resulted in only measuring one or more of these forces. Thus, Bischof added sand until the mixture was so soft that it could be rubbed away between his finger and thumb. Bischof's figures are, however, a measure of the binding power of the clay, but not of its plasticity. Measurements of tensile strength, viscosity, the amount of water required to produce a mass of given consistency, the consistency, or the depth to which a Vicat needle will penetrate, Sokoloff's slaking test and other single characteristics are all useful in their way, but they fail to include all the properties involved in the

use of the term "plasticity." Zschokke, who has examined the subject very fully, considers that the percentage of extensibility multiplied by the tensile strength of a freshly moulded clay cylinder of standard size (60 mm. high by 30 mm. diameter) is a coefficient of the plasticity. Modifications of this method have given excellent results in the hands of several experimenters in different countries and with a very large variety of clays. Grout considers that plasticity is proportional to the product of (*a*) the load required to sink a Vacat needle to a definite depth in a mass of clay; and (*b*) the deformation of the clay under stress, which he measures by the increase in area of a clay cylinder produced by a load which just causes cracks to appear. Both Zschokke and Grout[17] really consider plasticity to be measured by the product of the deformability and force resisting deformation, though they differ in the manner in which they measure these forces. More recently, Ashley[7] has adopted the same general idea as to the forces involved, but has assumed that the force-resisting deformation is exerted by the colloids in the clay. He, therefore, regards the plasticity of clay to be measured by the ratio :—

$$\frac{\text{Relative colloids} \times \text{the shrinkage of the clay}}{\text{Jackson-Purdy surface factor.}}$$

The term "relative colloids" is explained in the section on *Adsorption.*

As the ratio of the surface factor to shrinkage is approximately constant, Ashley concludes that the plasticity of the clay is directly proportional to the colloids present. The objection to this conclusion is that it appears unlikely, from other considerations, that the whole of the plasticity is due to the colloidal matter.

Rohland[5], also assuming that the colloidal matter in the clay is the chief factor of the plasticity, has suggested that the ratio obtained by dividing the coagulable colloids by the non-coagulable material is a measure of the plasticity. He ascertains it is by measuring the amount of water required to make the clay into the consistency of a good modelling paste, and argues that this is a measure of the colloids because as soon as sufficient water is present to dissolve the coagulable colloids, a saturation point is reached and no more water can be absorbed without the clay losing its stiffness.

Stormer has stated that plasticity may be judged by the following characteristics :—

(1) The proportion of water (absorption) which must be added to the clay to make a good modelling paste. This is not always reliable.

(2) The "feel" of the paste when rubbed between the finger and thumb (*binding power*).

(3) The behaviour of the paste when rolled up into a "sausage" (*toughness*).

(4) The adhesiveness of the clay (*adhesion*).

(5) Twisting a piece of clay into a spiral and noting its behaviour (*torsion*).

(6) Noting the length of the threads, produced by expressing the clay from a vertical pug mill, before they break off by their own weight (*tensile strength* and *extensibility*).

(7) Forming balls of clay and pressing them until the edges crack (*crushing strength*).

(8) Bending cylinders of clay into a ring (*bending moment*).

None of these characteristics taken alone can give a measure of the plasticity of a clay, though several of them are closely related to each other. The most reliable measure of plasticity appears to be that devised by Zschokke (p. 133) or by Rosenow, who multiplies Zschokke's figure by the percentage of water added to the dry clay to make it into a workable paste, *i.e.*, by Rohland's figure (p. 133).

The *binding power* of a clay is the property it possesses of uniting with non-plastic material and water to form a uniform plastic paste, and is consequently closely related to the plasticity. This absorption of non-plastic material with the spread of plasticity throughout the whole mass has been attributed to the power of the saturated colloids (gels) to retain the non-colloidal particles in a state of pseudo-solution. Other colloids are known to possess the property of preventing insoluble matter from settling, and this is, in some senses, a parallel case. The binding power of a clay may be determined by measuring the tensile strength of mixtures of clay with varying amounts of sand, but a skilled clayworker can tell by the "feel" whether such mixtures are strong enough to be useful. In order to determine how much lean clay or non-plastic material can be added to a clay without unduly destroying its value for moulding into shape, Bischof's test may be used. In this, the two materials are mixed in various proportions and the same measured quantity of water is added to each. The pastes are then rolled into small balls as equal in size as possible, and allowed to dry. They are then rubbed gently between the finger and thumb, or with a small "camel hair" brush. The mixture which just resists the action of rubbing may be taken as the standard. Some authorities make up balls of mixture in this way and then notice to what length a cylinder can be rolled from each without cracking.

Clays with a high binding power are known technically as "fat" clays; "lean" clays are deficient in binding power.

Some writers appear to consider that binding power and plasticity are synonymous; this is by no means the case, as a clay may be very plastic and yet not be able to bind much non-plastic material into a uniform plastic paste. At the same time, there is clearly some relationship between these two properties of clays.

The *dehydration of clays* is accompanied by changes which are remarkably similar to those which occur in the dehydration of colloidal gels. The most important of these changes is the shrinkage or contraction of the mass, the production of a hard material which—if the dehydration is accomplished by heat—may result in the production of a material comparable to an irreversible gel.

Plastic clays, like colloidal gels, shrink greatly when dehydrated and possess both a drying-shrinkage and a kiln-shrinkage. By mixing

an inert substance, such as sand, with a true colloid the shrinkage is lessened, and the cohesion of the dried colloid, including its adhesion to inert substances, are the causes of the increased mechanical strength of many such mixtures. This is another characteristic common to colloids and to all plastic clays.

As there is no wholly reliable method of measuring plasticity (*see* p. 124), it is not possible to state precisely what relationship exists between the plasticity and the shrinkage of clays. Speaking broadly, the most plastic clays shrink more than those which are less plastic, but this is not invariably the case. For instance, the Lias clays usually shrink less than would be expected from their plasticity.

When articles made of plastic clay are dried under suitable conditions, they contract equally in all directions, the contraction in volume being almost three times the linear shrinkage. Excessively plastic clays crack, or twist, when dried and many moderately plastic clays will do so if dried irregularly or too rapidly.

When water is added to a dry clay, it is first absorbed by the pores, but, when these are filled, any further supply of water appears to cause a separation of the particles from each other so that the volume of clay is increased, though not in proportion to the water added. The amount of water which can be absorbed in this manner differs greatly with different clays. The stage at which the clay contains the maximum quantity of water without loss of shape is also the point of maximum plasticity; it is said to be the "point of saturation of the coagulated colloids (gels) in the clay." If some of this water is removed, the volume of the mass begins to diminish and contraction occurs. This contraction or shrinkage is chiefly, but not entirely, due to the removal of water from the clay by evaporation at the ordinary temperature (air-shrinkage), at a somewhat higher temperature in the dryer (dryer-shrinkage), or during the burning (kiln-shrinkage).

As all coagulated colloids (gels) which are saturated with water shrink when the water is removed, some investigators consider that the shrinkage of clay may be due in part to this cause.

The more general idea (which states facts rather than explains them) is that, as the water is removed, any which remains draws the clay particles together into a smaller and denser mass.

The amount of shrinkage appears to depend partly upon the rate at which the clay is dried, for if this operation is performed rapidly the shrinkage will be less, the clay particles not having time to move over each other so freely as when the drying is slower. When drying a strong, porous clay, the water first evaporates from the surface and is replaced by capillary action from the interior, the mass contracting by the same amount as the water diminishes. All the pores remain filled with water until the rate of evaporation exceeds the rate at which the pores will transmit water. This point occurs, when the clay particles move so much less freely on each other that the rate of evaporation exceeds that of the contraction. After the first stage of surface-drying, the exterior loses water more rapidly than the interior; in the second stage the pores are no longer filled with

water at their outer ends and begin to form spaces in the clay, these spaces being filled with air and water vapour. Contraction still occurs throughout this second stage until the substance is so far solidified that the individual particles can no longer slip over each other at all. The third stage is then reached in which capillary action and shrinkage cease entirely. Evaporation now takes place entirely within the mass, and spaces are formed exactly corresponding to the water lost. That shrinkage ceases before the clay is completely deprived of water is shown by Aron and Brogniart to be characteristic of many, but not of all, clays. Aron supposed that the clay shrinks until the particles are practically in contact with each other, so that any further water which may be driven off does not make any notable difference in the volume of the clay; but supporters of the colloid theory argue that the heat used in drying really cause the colloid particles to shrivel, thus reducing their surface and increasing their density. Aron has further shown that the "pore space" is constant for each kind of clay, and is independent of the amount of water of formation added to the clay, though this last statement is only true of the purer clays.

If, now, the pastes made with varying amounts of water of formation are subjected to exactly the same conditions of drying, the rate is not proportional to the water added, but is slower in proportion for those with less water. It takes, approximately, the proportional time in the first two stages of drying, but the more solid the mass the longer it takes to eliminate the last portions of the water. It follows also from this, that want of uniformity in the substance of a mass of clay, such as must exist in bricks made by hand, and in a less degree in those made in a press or die, causes a corresponding want of uniformity in the shrinkage and the rate of drying in different parts of it. This is one cause of the warping or twisting of bricks in drying.

In the second stage of drying, all clays lose water more rapidly on the outside than on the inside, the angles and arrises in their turn drying more rapidly than the faces. The consequence of the greater shrinkage of the outer layer is a frequent cause of cracking, and it is, therefore, necessary to pursue this stage with great caution and to effect the drying with air already heavily charged with moisture. It is also essential, for this reason, to avoid the excessive prominence of any part of a complex-shaped article, and it is advisable to follow any projections on the exterior with hollows on the interior, so as to maintain an approximately regular thickness of material throughout. The frogs or indents on both sides of a common brick are serviceable in drying for the same reason. In a re-pressed brick, they serve the additional purpose of rendering the consistency more even throughout.

For objects of reasonable size, the rate of drying is approximately proportional to the ratio of surface to volume. Objects of large size, however, take much longer to dry, and require the application of considerable heat to complete the removal of all the water of manufacture from the interior. Many large goods made of fireclay and stoneware clay require extremely careful treatment, and have to be kept in a heated atmosphere for several days after the moisture

has apparently been completely removed. Disastrous results have frequently been known to occur in the steaming operations in the kiln for want of sufficient care in this particular. Manufacturers frequently adopt a very wise precaution in having such goods stamped with the date of making, and in holding their workmen responsible if they are rendered unsound by being burned before the lapse of a stated period of drying.

In order that the goods may not twist or warp when drying, it is essential that they should shrink very little. This means that only a limited proportion of plastic clay can be used in the material, although some is necessary to bind the particles together and to give it the general characteristics of "clay." With a carefully compounded mixture, the contraction of the paste prior to entering the kiln should not exceed 1 inch in 16 (or $\frac{3}{4}$ inch per foot). If it does so, more non-plastic material must be added. The lower the contraction, the better the chance of the ware coming "true" out of the drying rooms; hence, as much non-shrinking material as possible should be used in the clay mixtures, so as to keep the contraction at a minimum. The addition of a non-plastic material to a clay enables less water of formation to be used, and so reduces the shrinkage, but Aron has shown that if the amount of water is kept the same as for the clay alone, the addition of non-plastic material will increase the contraction which occurs on drying, until a certain point (that of maximum density) is reached. After this, the more "grog" added to the clay the less will it shrink, and the greater will be the porosity. The nature of the non-plastic material added will also affect the shrinkage to some extent, and will exercise a considerable influence on the amount of water which must be mixed with the clay. Thus, a porous, burned clay will absorb more water than will sand. Provided the non-plastic material is of a nature suitable to the clay (this must be determined by actual experiment), it may be added in any desired proportion so long as it does not too seriously reduce the strength of the mass, as it will do if more is added than the binding power of the clay can accommodate.

The porosity of a dehydrated clay appears to be due to the capillary structure of the material.

Other properties which clays in the plastic state possess in common with colloids are :—

*Unctuousness*, or a smooth, almost greasy, "feel," is a characteristic of some clays, a few being so oleaginous that they may be saponified by treatment with caustic alkali, the plasticity being thereby increased. In most cases, however, such treatment makes the clay more fluid.

*Toughness*, or cohesion, is closely allied with (1) *extensibility*, or the ability of clay to stretch when pulled, which is measured by ascertaining the fullest extent to which a clay test-piece of a given size will stretch without breaking; (2) *torsion*, or the extent to which a piece of clay can be twisted, which is measured by clamping one end of a bar of clay as rigidly as possible and rotating the other slowly by means of a screw, counting the number of complete revolutions which can be made before the bar breaks; (3) *bending moment*, or

the angle through which a bar of clay can be bent without rupture; (4) *elasticity*, or the extent to which a piece of clay can be stretched and yet return to its original length when the tension is removed. Many plastic clays show slight elasticity, though it is usually too small to be measurable.

The *tensile strength* of a clay is its resistance to torsion or to being pulled apart. The non-plastic materials influence its strength inversely as the diameter of their grains, so that fine-grained clays will usually be the strongest, though an excess of very fine or very coarse grains will cause the clay to break prematurely. In support of the theory that the grains of clay interlock to some extent, Ries found that mixtures of two clays can be made which have a higher tensile strength than either clay taken separately. This fact has long been known by the makers of crucibles for steel-melting in this country, as many as four different clays being sometimes used to produce a sufficiently strong crucible. The tensile strength of the clay has, in fact, an important bearing on its resistance to accidents in the process of manufacture, particularly from the commencement of drying to that of firing. It has sometimes been stated that the tensile strength of a clay enables it to carry a large quantity of non-plastic material, but this is rather confusing the effect with the cause. It is the binding power of the clay which enables it to carry such a large quantity of added material and still retain a sufficiently high tensile strength. Olschewsky has proved that there is no direct relationship between the binding power of a clay and its tensile strength when dry. It was at one time thought that the tensile strength of clays is proportional to the plasticity, but this is only true, if at all, when the pieces are tested in the moist (plastic) state. If air-dried, the definite relationship ceases.

The tensile strength of dried raw clays depends on the proportions of the grains of different sizes. Equal-sized grains cannot be packed into a dense mass. An excessive proportion of the finest clay particles or a large percentage of sand grains (0·5–1·0mm.) weakens the strength of an air-dried clay.

*Fissility*—or capability of being split up into thin slabs or flat pieces, or even into flakes or foliations—is characteristic of many indurated clays, especially of shales. If the splitting can be effected so as to form plates of extreme thinness, the material is said to be *laminated*; if the tendency to split is strongest in the direction of bedding, the material is termed *shaley*; if this tendency is strongly marked in any other direction it is said to be *fissile*, as are slates and certain limestones and sandstones.

*Sectility*, or capability of being easily cut, is a characteristic of clays which occur in a plastic condition, such as ball clays and many surface clays. This property often serves as a means of distinguishing "clays" from other minerals, though the "clays" so found may be too impure to be of any commercial value. Anyone constantly engaged in examining clays soon learns to recognise some varieties by their sectility and by the slightly glossy appearance of the freshly-cut surfaces, though these cannot be clearly described.

*The effects of age* on a clay paste are similar to those on colloidal gels, provided the conditions of storage (including the low temperature and a sufficiently humid atmosphere) are favourable. The plasticity of the clay is slightly increased and the colloidal properties are more marked.

From the foregoing, there appears to be a close parallelism between the more important properties of plastic clays and those of other colloids, but the question still remains as to whether these colloidal properties are due to the nature of an essential constituent of clays (clay substance) or to other colloidal substances which may be present.

### *Other Colloids in Clay.*

The most important colloidal substances which are known definitely to exist in some clays are :—

*Colloidal silica*, which may exist in the form of a silica hydrogel, with or without occluded silica hydrosol, the latter being confined to any liquid portions of the clay paste, but distributed more or less uniformly throughout the clay slip. Various mineral forms of silica which are hydrogels are known; they possess the anticipated properties of inorganic gels and their nature is fairly well known. A small percentage of colloidal silica may be extracted by boiling some clays with water, with or without the addition of a little sodium carbonate, but in no clay of commercial importance is the amount of silica obtainable so large as to account for the whole of the plasticity of such clays, though it may partly do so.

Wolfgang Ostwald[19] holds the view that silicic acid sols are hydrated *emulsoids*, *i.e.*, the dispersed silicic acid is a liquid and not a solid. Like other known emulsoids, its viscosity is high and rises very rapidly after a given concentration whilst in suspensoid sols the increase of viscosity is steady throughout and the viscosity is very low. He also states that the silicic acid gel differs from the better known organic emulsoids in possessing little elasticity.

Attempts to increase the plasticity of sand by mixing it with silica hydrosol, and coagulating the latter, do not produce a material at all closely resembling plastic clay. Such a mixture, when dry, is deficient in strength and even in its most plastic state it is inferior to clay for modelling purposes. A still more striking difference between such a mixture and a clay is that when both are dried at 105° C. and afterwards mixed with water, the clay forms a plastic paste with all its original modelling power restored, but the silica-sand mixture is not " workable " or truly plastic.

Silica gels have a peculiar property of varying according to their age as well as according to the mode of formation. When a clay is soured, the proportion of silica gel tends to increase, but if soured too long the silica gels grow together forming larger particles and cause a diminution in the plasticity of the mass, the vapour pressure in the old gel being greater than in the new one.

A. Cushmann[18] found that the addition of dried colloidal silica gel to a dry clay, the mixture being afterwards made into a paste

with water, increased in binding power and shrinkage, but not in plasticity, whilst colloidal alumina, when similarly treated, increased in plasticity but not in binding power and shrinkage. A mixture of colloidal silica and alumina, made by adding a solution of water-glass to one of alum, increased both the binding power and the plasticity of a clay. Grout repeated this experiment, but obtained a negative result.

On drying the silica gel, the volume decreases to a characteristic point (Van Bemmelen's[19] "transition point"), after which it remains constant. On further dehydration, the clear gel becomes turbid and eventually chalk white, but becomes clear again when the water content is reduced to less than one molecule. The addition of water causes little change in volume. At low red heat the gel is completely dehydrated and strong ignition prevents the gel from again taking up water. Any salts present cause the gel to lose its power of taking up water more rapidly. Salts are also favourable to local fusion and destruction of the gel. These characteristics are equally characteristic of plastic clays.

*Colloidal alumina*, of which a small and variable proportion occurs in many clays, especially those known as *laterites*. Colloidal alumina has a very curious and variable effect on the clay. In some cases, it behaves as an acid easily combining with bases to form salts, whilst under other conditions it acts as a base combing with acids. It is soluble in both acids and alkalies forming different compounds in each case. The gel has a particularly low water content, having only about $2\frac{1}{2}$ per cent. more than is required to form the hydrate, a fact which is very unusual, as most mineral gels have a very large proportion of free water which can be removed on drying. In most of its physical properties, such as shrinkage, swelling power, &c., it is similar to silica.

Mixtures of sand and alumina hydrosol, treated so as to coagulate the latter are somewhat plastic, but would not be acceptable to clayworkers as a substitute for plastic clay.

*Colloidal Ferric Hydroxide* has been isolated in very small quantities from some ferruginous clays, but clearly cannot be an important cause of plasticity in clays which are almost free from iron compounds. Like silica, ferric hydroxide sols increase in viscosity with the concentration. The surface tension of ferric hydroxide sol is the same as that of water and the electric conductivity was observed by Malfitano to be $200 \times 10^{-6}$.

Colloidal ferric hydroxide particles carry a positive charge, *i.e.*, that opposite to that of colloidal silica, so that the two substances mutually precipitate each other. This accounts for some siliceous minerals and clays having a thin coating of iron which also partially fills the interstices. A very peculiar fact with regard to colloidal ferric hydroxide is that it is entirely free from the inky taste which is so characteristic of ordinary iron compounds, and it has no reaction with potassium ferrocyanide (the Prussian blue test which is the most characteristic test for iron), whereas yellowish china clays when treated with ferrocyanide become whiter owing to the Prussian blue

colour being complementary to the yellow tinge caused by iron compounds in the clay. The proportion of water present in colloidal ferric hydroxide is very variable; it parts with water on drying in a similar manner to silica though it is much more irregular. The variable proportion of water probably explains the variable colour to different clays containing iron compounds.

Various *colloidal silicates* have been found in small quantities in some clays, though absent in many highly plastic clays. The only exception to this is a possible " silicate of alumina " or more correctly " alumino-silicic acid " (or series of such acids), which appears to be an essential constituent of clays and may be the origin of the colloidal substance to which they are supposed to owe their value.

*Colloidal organic matter*, chiefly humus, may play an important part in giving to clays their characteristic properties, but as some well-known highly plastic clays are almost devoid of carbonaceous matter, the latter cannot be the chief cause of their plasticity. Moreover, the addition of certain organic colloids to feebly plastic clays does not increase their true plasticity, though it may increase the cohesion and stickiness of the particles.

From the foregoing it may be assumed that the characteristic properties of clays are not due to colloidal silica, alumina, ferric hydroxide or organic matter, or to colloidal silicates of the alkalies or alkaline earth metals, though when any or all of these are present they may slightly increase the plasticity, or otherwise modify the properties of the clay.

### *To what Colloidal Matter do Clays owe their Character ?*

It has been suggested in the foregoing pages that the more important properties of clays may be due to the presence of colloidal matter in them. It has been shown that colloidal matter does exist in clays and that many of the characteristic properties of clays are equally characteristic of colloidal gels, though none of the latter possess all the properties of a valuable plastic clay. The question therefore arises, as to whether the so-called colloidal properties of clays are merely coincidental with the composition of clays, or whether plastic clays contain some substance or substances not hitherto identified as a colloidal gel.

There can be no doubt that most plastic clays contain a large proportion of non-plastic and non-clayey material and may be regarded as diluted clays. Some of the most highly plastic clays, on the contrary, consist of such small particles that the non-clayey matter cannot be satisfactorily separated. On the one hand, attempts to separate an ideal " clay substance " by chemical or mechanical methods have resulted in a material which is almost devoid of plasticity, and on the other, attempts to show that clays are essentially colloidal have not satisfactorily produced any definite colloidal substance which can be regarded as clay. We are, therefore, compelled to realise that many of the more important properties of clays are due to the colloidal nature of the material, though clays are not wholly

colloidal, and that this essential colloid has not been identified. In so far as it does exist, it appears to be (*a*) a colloidal alumino-silicic acid widely distributed through a mass of inert granular material of the same chemical composition or even of an entirely different one, such as sand, the whole being comparable to a freshly-made concrete, but differing from the latter in requiring heat to "set" it. Alternatively, (*b*) the colloidal material may be a mixture of colloidal silica and colloidal alumina precipitated simultaneously from the sol state in such a manner as to appear to be a definite chemical compound. This possibility can only be confirmed or disproved by a large amount of experimental work which is not yet completed. The chief difficulty in accepting the alternative hypothesis is that, if it were correct, it should be possible to isolate relatively large quantities of colloidal silica and alumina from such highly plastic and relatively pure clays as the ball clays, but this has not been accomplished. This may be rendered difficult or impossible by the mutually coagulated silica and alumina gels behaving as a compound in which the silica and alumina have so great an affinity for each other that they cannot be separated by means applicable to the isolation of the simpler gels. Finally, (*c*) as almost any material may, by suitable treatment, be converted into the colloidal state, the characteristic properties of plastic clays may be independent of the chemical composition of the colloidal matter present in them. If this were the case, any mineral substance which could be converted into colloids by the natural agencies to which clays had been subject would be possible sources of clay. This explanation has the great advantage of explaining the small proportion of colloidal matter present in even the most plastic clays, as if such colloidal matter were the result of age-long grinding of minute rock particles under water, it is only natural to suppose that the product of such action would be grains of the original rock surrounded by a film of colloidal material. If, on the contrary, clays are produced by mixing colloidal matter (formed separately) with non-plastic grains, it is most likely that considerable quantities of such wholly colloidal matter would be found in small pockets or fissures in clay beds. This does not appear to be the case.

If any or all of these three alternatives were correct they would explain many of the known properties of clays. Both silica and alumina gels readily become irreversible; even when prepared under the most favourable conditions they are much less "manageable" than many other colloids. Hence, it is only to be expected, that if a complex gel containing both silica and alumina in intimate admixture or even in a state of combination would be extremely difficult to isolate in an approximately pure state.

The conditions, under which clays are formed from felspar and other silicates, are so varied, that they do not throw much light on the nature of clays. China clays in Cornwall appear to have been formed by the action of water and acid vapours on granite at a high temperature, the felspar present being decomposed into soluble potassium silicate which has, presumably, been removed in solution, insoluble quartz and clay, the clay being readily separated from other

detritus by a slowly moving stream of water. This explanation—though widely accepted—is by no means satisfactory, and if it is assumed to account sufficiently for the low degree of plasticity of china clay it does not explain the high plasticity of Devonshire ball clays not many miles away, unless the latter are presumed to have no connection with the Cornish clays. Rohland[5], on the contrary, attributed the low plasticity of some kaolins to the colloidal clay having been largely removed in the sol state.

So far as can be ascertained at present, the colloidal material to which clays appear to owe their characteristic properties has been produced by the very prolonged action of water on rocks, chiefly those composed of one or more alumino-silicic acids, the precise nature and origin of which is still uncertain, though represented roughly by the formula $H_4Al_2Si_2O_9$ in the case of Cornish china clays, Dorset and Devonshire ball clays, and possibly of other less pure clays. This colloidal constituent of clays appears to be a very finely divided, solid cellular substance* which can absorb water like a sponge and thereby form a kind of jelly which retains the water by capillary attraction and only permits it to evaporate very slowly at the ordinary atmospheric temperature. Consequently, the proportion of water present in a clay paste of given consistency is a rough measure of the colloidal matter present and when precisely similar clays are compared, it may also be a measure of the plasticity of the paste; the latter property is partly due, however, to the size of the grains coated by the colloidal material and by the thickness and other physical characteristics of the colloidal coating and the extent to which it penetrates any pores or interstices in the granular material. If such a colloidal material were isolated, it would apparently be peptised by a dilute solution of alkali, or by lime water, and recoagulated by strong acids. On heating, it would first contract greatly and simultaneously part with a considerable part of its absorbed water. On further heating up to 500° C. or above, it would be decomposed with the evolution of water and the formation of an irreversible material largely colloidal in character, though different in many ways from most well-known colloids. On further heating,it might undergo other changes, the nature of which can only be summarised as including polymerisation, but one product which under favourable conditions may be expected to be formed is crystalline sillimanite, $Al_2O_3Si\ O_2$. When heated with caustic alkalies, bases, and most metallic oxides, the colloid would probably form mixtures of the corresponding silicates and aluminates. The colloid alone would probably be highly resistant to heat, but in the presence of a metallic oxide (other than alumina) it would fuse more readily.

It is comparatively easy to obtain colloidal silica from calcined, and therefore irreversible, or from the crystalline forms of silica, but the process is so drastic (including the fusion of the material with sodium carbonate) that it appears inapplicable to clay, as the latter is completely decomposed during the heating with the flux and the final colloidal product is merely a mixture of colloidal alumina and

* It need not, of course, consist of any one chemical compound; even if it consisted chiefly of one such compound, it would seldom, if ever, be pure.

silica which does not possess the properties of the original clay. Various other attempts to synthezise " true clay " have been equally unsuccessful.

It is generally considered that one of the most important sources of clays is the mineral felspar which can be obtained in the form of pure crystals, should form a good starting point. The felspar to which certain clays are commonly attributed is orthoclase, which has the formula $K_2Al_2Si_6O_{16}$. This is a minimum formula and may be more correctly represented by $K_{\times}Al_{\times}Si_{\times 3}O_{8\times}$. Keeping the simple form, the decomposition may be represented by—

$$K_2Al_2Si_6O_{16} + 3H_2O = 2K_2O + H_4Al_2Si_2O_9 + 4SiO_2,$$

which assumes that the felspar is a potassium alumino-silicate with china clay as the corresponding acid, but containing much less silica. Fireclays, on the contrary, even after such limited purification as can be effected, often contain more silica, and indicate a slightly different equation and they appear to have an entirely different origin both chemically as well as geologically. Unfortunately, this decomposition of felspar has never produced clay when carried out in the laboratory. Water produces under great pressure a white body which has little or no plasticity, which may be clay, but cannot be identified as such.

Another attempted synthesis was that of Pukall,[20] who decomposed a pure china clay with sodium chloride and treated the product with carbonic acid. It then yielded a salt deficient in silica and soda and corresponding to $2Na_2O\ 4H_2O\ 6Al_2O_3\ 10SiO_2$. The same salt when treated with a strong acid (HCl) dissolves and from the solution ammonia precipitates a material which Pukall mistook for synthesized clay, but which contains rather more hydrogen and oxygen and dehydrates readily at 350° C. instead of 500° C. Apparently, an isomer of clay had been formed.

At present, it seems quite impossible to be certain of the composition of the substance or substances to which clays owe their chief characteristics. The reporter favours the view (p. 125) that age-long grinding has produced a film of colloidal matter on grains of non-plastic material as probably accounting for most clays, but he also believes that no single cause can account for the formation of all kinds of clay, and that other explanations, such as those given on p. 126 *seq.*, may be equally correct in some cases. The fact that the finer particles of all plastic clays correspond more or less closely to the formula $H_2Al_2Si_2O_9$ does not necessarily invalidate the theory that clays are simply a product of intensely ground rocks, as there are many clays which do not correspond to the formula just mentioned and some of these which correspond to it more closely are only feebly plastic. The similarity in composition of materials regarded as clays may, possibly, be merely a coincidence due to the predominating proportion of alumino-silicious rocks in the material of which the earth's crust consists.

Whatever its nature and origin, it is now fairly well established that many of the properties of clays are closely connected with the colloidal matter present, such matter being in the form of a film of

colloidal gel surrounding particles which are of a non-plastic or colloidally inert nature; in some cases, they may be rich both in alumina and silica—as in china clays and ball clays—whilst in others they may be almost wholly silicious, as in fireclays and many brick earths.

The particular kind and amount of gelatinous matter present, the size and shape of the grains of non-colloidal material, and the relative proportions of large and small grains are important factors in determining the various physical properties of clays, particularly their binding power, compressive strength, tensile strength, and air shrinkage.

*Some Technical Uses of the Colloidal Properties of Clays.*

Although the nature of the materials to which clays apparently owe their colloidal properties is unknown, great use is made of the properties in various industries, as will be seen from the following notes :—

In *purifying clays* and similar substances, the suspension of the material in water, followed by a process of elutriation or sedimentation, whereby the coarser impurities are removed whilst the partially purified clay is carried off in suspension, has been in use since ancient times. More recently—especially in America—electrolytes, such as sodium carbonate, caustic soda, &c., have been added to the water employed, so as to ensure a maximum amount of clay being held in suspension in a minimum quantity of water. The use of such electrolytes also ensures a sharper separation of the inert sandy material present. The suspension is run off into suitable vessels, the added alkali neutralised by the addition of sulphuric acid; the clay is allowed to deposit and afterwards removed and dried. The separation of the impurities is due to the fact that whenever a charged colloid particle in suspension meets another similarly charged particle they mutually repel each other and so remain in suspension. When two particles of opposite charge come into contact, the charge is neutralised, and the two particles unite and are precipitated. The electrolyte added must, therefore, be one which will increase the negative charge of the material as a whole, so as to effect the precipitation of the impurities, (which are chiefly electro-positive) and retain in suspension the electro-negative particles of clay and, along with them, some silica which is also electro-negative. The coarser particles of silica, pyrite, felspar, mica, &c., do not become charged, but settle on account of their size and weight. If the liquid is too viscous, the impurities will not settle properly, and it must then be diluted until the density and viscosity are such that sufficient separation is effected without the loss of clay by sedimentation.

A similar process of purification is used as a preliminary stage of the Schwerin electro-osmosis process[21], but instead of the clay being allowed to settle it is caused to migrate to a rotating electrode immersed in the liquid and is scraped off in the form of a stiff paste. Schwerin found that all clays did not behave thus, and only migrated so when they carried an electric charge. This charge is supplied,

in some cases, by the addition of organic colloidal matter, such as humic acid prior to the use of alkali.

The apparatus for treating clays consists of a wooden trough with one electrode of wire gauze, and the other a metal drum rotating in the trough containing the alkaline clay slip. The electric current is then passed through the fluid, using the gauze and drum as poles. In this apparatus, a further slight purification is effected owing to the tendency of the impurities to travel to one electrode whilst the clay (with some silica) travels to the other. The clay and finest silica particles assume a negative charge, but that of the silica is so slight that the silica remains almost stationary in the fluid, whilst the clay travels to the anode. Pyrite, alumina and ferric oxides are positively charged and travel with the water towards the cathode. The dominant feature in the speed of migration is the valency of the material attracted to the diaphragm.

The chief use of the electro-osmosis process is for producing a clay paste sufficiently dry for commercial purposes, as the greater part of the purification is effected before the current is applied.

The electro-osmose process whilst theoretically interesting, is not, at present, regarded as of much practical importance, as the use of electricity to separate clay and water is more costly than other equally efficacious methods. Moreover, the finest particles of free silica migrate simultaneously with the " true clay " so that only a very limited purification by the electric current is possible, the greater part having been done by the electrolyte added, which is not an essential part of the osmosis process.

In East Germany, it has been used for some time on a commercial scale, and about two years ago an English syndicate was formed to exploit the Schwerin patents, and to supply certain requirements of the Optical Department of the Ministry of Munitions. For further information on the electro-osmose process for the treatment of clays *see* " The British Association Report on Colloids, II, 1918," pp. 42–4, 47–52.

A possible method of purifying clay and separating the colloidal silica is due to Billitzer (1905), who found that in N/2 to N/10 solutions of hydrochloric acid, the charge of colloidal silica is changed from electro-positive to electro-negative so that the careful addition of acid should enable a practical separation of colloidal silica from colloidal clay to be made. The importance of this suggestion appears to have been overlooked.

*In separating clay and water*, as when it is desired to dry a clay slip or suspension, use may be made of the electric and colloidal properties of the clay. This is an essential feature of the Schwerin electro-osmosis process[21] previously described. On passing a current of electricity through the clay slip, the clay migrates to, and is retained by the rotary electrode (anode) and the water tends to travel to the cathode, so that the clay removed from the drum is drier than from a filter press worked at a pressure of 150 lb. per sq. inch. Thus, some ball clays may be obtained with only 17 or 18 per cent. of water, and so dry that it cannot be pugged, whilst the same clay,

when removed from a filter press would not contain less than 30 per cent. of water. The clay acts like a porous diaphragm made of capillary tubes and this shows the well-known phenomena of endosmosis.

*In making articles* of clay and allied materials by the casting process, *i.e.*, by pouring a suspension of the materials into a mould and, after a suitable time, pouring off the surplus fluid, it is important to have as concentrated a suspension as is reasonably possible. When water is used, only moderate concentrations can be used, but by adding a small percentage of a suitable electrolyte such as sodium carbonate or water-glass, or both, the amount of clay in suspension can be doubled and the casting process greatly facilitated. This use of an electrolyte, is based solely on the assumed colloidal nature of the clay. Care must be taken in choosing the electrolyte, as some substances such as sodium carbonate if used alone will cause a very high surface tension, with the result that the slip "balls up" and may cause the inclusion of air bubbles, whilst sodium silicate used alone causes the clay to flow in "strings" like a thick syrup. A suitable mixture of the two, however, is excellent, and gives a smooth flowing stream without any tendency to the defects just mentioned. Slips containing a suitable electrolyte require far less time in the mould than those slips in which plain water is used. This is necessary in consequence of the smaller proportion of water present and is of great practical importance as it reduces the number of moulds required. With a good stoneware slip containing soda, a mould may be used five or six times in succession without drying and with slips of leaner clays, the moulds may be used still more frequently. On the other hand, the salts absorbed by the plaster tend to make the moulds less durable when soda is present in the slip.

A slip to which soda or other electrolyte has been added feels more soapy and plastic than one with plain water; on passing it through a sieve, it does not flow so readily and tends to form long syrupy strings, and, on long standing, little or no separation occurs. A soda-slip also flows more steadily and with less tendency to include bubbles of air than one made without an electrolyte and the painting of portions of a mould with slip, which is sometimes essential to ensure the production of a good surface on the ware is entirely unnecessary when a suitable electrolyte is used.

*In increasing or reducing the plasticity* of a clay or earth, so as to make it suitable for the manufacture of various articles, the methods most extensively used are based on the assumed colloidal properties of the clay. Plasticity is increased by methods (p. 130) which increase the amount of colloidal gel in the material and it is reduced by the methods (p. 131) which will lessen the amount of irreversible colloid gel, or by converting it into a hydrosol. Thus, the processes of *ageing* and *souring* the clay are dependent on an increase of colloidal matter by the prolonged hydrolysing action of the water on the clay, followed by a fermentation or acid-producing action which coagulates any hydrosols previously formed.

*Weathering.*—The reduction of large and hard masses of clay and shale is often greatly facilitated by exposure to weather, *i.e.*, to the action of air, sunshine, frost and rain. When so exposed, many clay materials disintegrate rapidly and may afterwards be made into a plastic paste much more easily than by any mechanical process of grinding and mixing with water. Different clays and shales are affected differently by exposure; some disintegrate after a few hours' exposure on a warm day, whilst others appear to require a succession of frosts and rainy periods. In most cases, the most feasible explanation of the physical changes which occur is that the conditions of exposure result in the partial peptisation of the colloidal cementing material which binds the particles of clay together. It is well known that sand grains soaked in concentrated glue and then suitably dried, form a hard rocky material which, on exposure or soaking in water, falls to powder as the colloidal element absorbs water, swells, and is no longer able to hold the particles together. It is suggested—though no definite proof is available—that when natural clays are exposed to weather a similar absorption of water by the colloidal matter occurs, and is followed by a corresponding disintegration of the mass. In the case of some clays, a certain amount of chemical change such as the fermentation of organic matter, or the oxidation of the pyrite, &c., also occurs and may also facilitate the disintegration, but the chief cause of the reduction of the material to a more or less pulpy mass, bears a much closer resemblance to the softening of the colloidal cementing mass than to any ordinary process of oxidation or other obviously chemical reaction.

Commercially, the weathering of indurated clays is of great importance, as it not only reduces the cost of grinding and mixing, but the weathered product is much more homogeneous and the water present is far more uniformly distributed than when the treatment of the clay is purely mechanical.

According to W. Taylor, the colloids produced during the weathering are *not* amorphous alumino-silicates, but *mixtures* of single gels produced by the mutual precipitation of positive and negative sols.

The ancient practice of storing clay in cellars for a long time, and known as *maturing* or *ageing*, is now seldom practiced to anything like the extent to which it was formerly thought necessary. Where hollow goods of very fine quality are made there is an undoubted advantage in thus storing the clay before it is made up into goods, but the keeping of clay in air-tight boxes for several years, as practised by the Chinese and more recently by Wedgwood and other famous potters, is no longer considered essential, though its beneficial effect on the clay cannot be denied. In Germany, the use of sumps, in which the clay and water remains in contact with each other for a considerable time, is still regarded as necessary.

In freshly pugged paste, there is only a limited amount of colloidal matter in an active form. Its amount may be increased by subjecting the paste to conditions under which any dry and horny colloidal gel will absorb water, swell, and form a soft friable jelly, and the same

result is obtained when a clay paste is stored in a cool place in a moist atmosphere for a sufficiently long time; the requisite coagulation occurs when sufficient acid is added to the material. This acid may be produced internally by the putrefaction of the organic matter, or it may be added artificially.

The swollen gel produced on prolonged storage is very permeable to water, and its structure may be compared to a series of solid grains wholly surrounded by liquid films which are not sufficiently thick to allow the particles to separate from each other or to flow appreciably. Such a structure has a powerful capillary action and consequently, it affects the distribution of water through the mass in a most thorough and efficient manner. This uniform distribution of the water largely—in conjunction with the coagulating and swelling of the colloidal matter—accounts for the increased ease with which an old clay-paste can be manipulated. The water in freshly pugged clay cannot be so uniformly distributed as when such a paste has been allowed to stand for several weeks, during which time the water is distributed through the mass by capillary attraction.

A much shorter storage of the clay paste, frequently in open sheds the material being covered with wet sacking, is known as *souring*. Its effect is undoubtedly to increase the active, as distinct from the dormant, plasticity of the clay, though there is a great variation in the extent to which this takes place. There is a widespread impression that souring is the result of bacteria or ferment-organisms, and some potters added sugar or honey to the clay to assist the fermentation but, whilst this may account for some of the observed effects, the hydrolysing action of the water present in the mass on the clay, silica, and iron hydroxide particles must not be overlooked. Rohland[5] suggested that the fresh clay paste is slightly alkaline owing to the felspar, &c., present in the clay being hydrolysed and converted into the colloidal form. The acids produced by the decomposition of any organic matter also present neutralise the cations; and the excess of hydrogen-ions produced coagulates the colloid matter and correspondingly increases the plasticity of the clay. This explains why the old vinegar " tip " of bygone potters develops the plasticity. Previous to this, Seger[1] had found that clays which remain alkaline do not increase in plasticity on storage, but do so if they are acidulated with acetic acid.

As heat is a disadvantage, souring must usually take place in a cool, moist, shed or cellar, if it is to be really effective; though in opposition to this, it may be noted that slips which are dried by heat are often more plastic than those treated in a filter press.

Some firms apply souring or storage to clays which are highly plastic, not to develop more plasticity but to secure a better distribution of moisture through the mass, and, as they express it, " to bring it into a better and tougher condition."

The weathering of crystalline minerals generally yields gels or mixtures of gels; thus, talc is formed from the weathering of serpentine, and some forms of brown iron ore from yellow ochre, but this is not invariably the case. It is, therefore, possible that

some clays may be mixtures of gels whilst others are mixtures of colloidal and amorphous alumino-silicic acids.

The customary arrangement of the paste in the souring shed is to fill a large clean floor with the paste to a height of about 5 feet, cover it with wet sacking and keep the latter moist for the desired duration of the souring. As fresh clay is added to one part of the floor, the soured clay is removed from another. Where the output is sufficiently large, it is convenient to use an annular building with 12–20 entrances as the addition of fresh paste and the removal of the soured paste may then proceed continuously with a minimum of trouble and space. In some works, the clay is stored in the form of balls or blocks about 3 feet diameter. If the paste is allowed to sour in wagons, each holding about 1 ton, a considerable amount of labour is avoided, though the gain is largely counterbalanced by the cost of the wagons.

During the souring period, the paste must be kept moist and special care should be taken not to allow a dry crust to form on its surface.

Air as well as moisture is necessary for the effective souring of some highly plastic clays, as the desired decomposition of the organic matter cannot occur in the absence of air.

It is very important to cover the clay to be soured, with wet sacking, as if this is not done the plasticity will be decreased instead of increased. In time, the union of the particles and also the growth of larger particles at the expense of the smaller ones may occur. Both may lead to the enlargement of the interstices between the grains and to the solidification of the gel residue, by which the total volume of gel remains fairly constant under constant tension. Crystallisation and other processes which enlarge the interstices during ageing also increase the vapour tension. During ageing the total surface of the particles is reduced, but the interspaces grow larger. This indicates that ultramicrons grow at the expense of the amicrons.

The duration of the souring period varies greatly in different cases. In some cases, only a couple of days is allowed; six to eight weeks is much more valuable when practicable, and the ancient makers of some Chinese porcelains are understood to have kept their paste for a hundred years! It is by no means unusual for the clay to be soured as much as six months and in exceptional cases, several souring periods are arranged. In making glass-house pots, for instance, the clay, is allowed to sour after a preliminary treading; it is then re-trodden, again allowed to sour and finally is re-pugged before it is ready for use.

*Increasing the Souring Effect.*—As the results which occur when the paste is allowed to sour are so beneficial, it is obviously advantageous to develop them as much as possible. The chief methods of doing this are :—

(i) To increase the amount of organic matter in the paste and to secure a more intense souring action. For this purpose, various putrefactive organic solutions such as wine, old vinegar, sewage, peat extract and also solid organic substances such as chopped vegetable matter, tannery waste, and even molasses

are sometimes used instead of plain water in pugging the clay. Such additions do not usually increase the plasticity of the clay to more than a small extent and they greatly increase the difficulty of burning the ware satisfactorily.

(ii) The addition of weak acid such as acetic acid, oxalic acid, or tannin (gallotannic acid) to neutralise the acid present or to discharge any hydroxyl-ions formed by the dissociation of salts present as impurities in the paste. One of the most interesting proposals in this connection is that of Acheson and Ries who have found that on the addition of a 2 per cent. solution of tannin to certain clays the plasticity may be greatly increased and the clay was apparently deflocculated and broken up into smaller particles, whilst the tensile strength was greatly increased. The use of a substance definitely known as an acid is not necessary; any substance which acts as a corresponding electrolyte of either organic or inorganic nature is advantageous because it neutralises the charge on some other electrolyte present in the paste and so effects a definite increase in the plasticity of the clay.

The great importance of souring is not appreciated as it should be, because the phenomena which occur are largely misunderstood and consequently, it is often omitted where it would be most useful. In the manufacture of bricks, and coarse goods, omission may not be serious, but it should never be omitted in the preparation of a paste for the manufacture of tiles, glazed ware, earthenware, fine pottery, and poreclain.

Ware made from a properly soured paste is less sensitive to sudden changes of temperature, can have thinner walls, does not break so easily, and is easier to produce as the souring increases the plasticity of the paste.

It is usually necessary to pug the paste after it has been soured so as to form it into a compact and homogeneous paste.

Certain clays have long been used as *absorbents* for grease and similar materials especially in fulling cloth and for medicinal purposes. Curiously enough, these clays are among the least plastic. Their usefulness depends on their absorptive and adsorbent properties.

Conversely, the use of clay in the preparation of *ultramarine* depends partly on its chemical composition, but chiefly on the colloidal nature of the product.

It should be remembered that clays can only be used for removing basic dyes and colours such as malachite green, as their removal from solution depends on the negative electric charge carried by the colloidal particles in the clays. Incidentally it may be noted that clays containing much colloidal silica or colloidal alumina give uncertain results when treated with malachite green.

Clays are also used in the preparation of several other colloidal substances including *Portland cement.*

The *clarifying power* of clays, when mixed with turbid fluids, also depends on the colloidal nature of the finely suspended particles

coalescing with, or being entangled with, the coarser particles of clay and being carried down by the latter. For this purpose, the clays should not be too finely divided, nor should they be highly plastic, as a somewhat coarser, porous material is more efficient and settles more readily. It must, however, possess sufficient power of adsorption to retain the finely suspended particles which cause the turbidity in the fluid which it is desired to clarify.

The use of clays as clarifying agents is particularly successful in the treatment of slightly oily effluents of spinning works, wool-scouring plants, distilleries, tanneries, dye-works, glue-factories, breweries, and other industries producing an effluent containing organic matter in a very finely divided or colloidal state. The best results are obtained when the colloidal matter in the effluent carries a positive electric charge as it is dissipated by the added colloidal matter bearing a negative charge. Domestic sewage, however, is not of this character, and, therefore, cannot be clarified in this manner. This fact confirms the essentially colloidal nature of the active ingredient in clay used as a clarifying agent.

The separation of water from clay in *filter presses* may, according to F. Ulzer[22] be facilitated by inserting suitable electrodes in the filter chambers, so as to coagulate the colloidal material and yet keep it from blocking the cloth.

The *extrusion of clay* through dies is made more rapid by the application of an electric charge, as described in " British Association Report on Colloids, II.," 1918.

The *binding power* of clays, like that of dextrin, gelatin, and other well-known colloids is used for uniting other particles into a compact mass as in the manufacture of refractory materials from non-plastic materials, " lead " in lead pencils, &c. Conversely, use is made of the colloidal property to reduce the excessive shrinkage of certain clays by the addition of suitable non-plastic materials.

In *agriculture*, the colloidal properties of clays play a most important part. It is now generally agreed that plants and other organisms growing in the soil, derive their sustenance chiefly from a film of colloidal matter surrounding the particles of inert material constituting the bulk of the soil and occupying some of the interstices between these particles. The soluble salts extracted from the mineral material in the soil or subsoil, or added in the form of a fertiliser, are adsorbed by this film of colloidal matter and transferred to the plant-roots, &c. There are several different substances existing in the colloidal state in soils, the more important being the colloidal " clay," silica, alumina, ferric hydroxide, and a mixture of partially decomposed organic substances collectively known as " humus." The last-named acts as a protective colloid for other substances, and absorbs many soluble salts. In association with other colloids, it determines the amount of water retained by the clay. Humus is negatively charged and is, therefore, coagulated into a gel by basic substances, such as lime.

The colouring matter in swamps is generally positively charged, and is, therefore, precipitated by colloidal clay. Alkaline humates are not colloids, but soluble substances. Being a negative colloid,

humus is precipitated by cations such as Ca, Fe, or Al which alter its permeability, absorption, and the way in which a soil "works." Fertilisers convert the silica gels into sols which rise by capillary action, and are again gelated nearer the surface of the ground or in the cells of the plants which absorb them. For further details, *see* "British Association Report on Colloids, II.," 1918, pp. 70–81.

In the manufacture of *detergents*, the use of clay has been developed to some extent on account of its colloidal properties, apart from its use as a filler.

It is well known that the amount of active colloidal material in clays can be increased by the addition of a certain proportion of alkali, which disperses the particles of clay, as shown on p. 119. F. E. Weston[23] made use of this fact in order to bring china clay into a highly colloidal state, and claimed that the colloidal clay thus formed could be used as a substitute for soap. His results are not, however, conclusive, and the clay-soap can only be used in special cases. It is of little value in toilet preparations, but as a substitute for the coarse soaps used in wool scouring it has been used with success, and several preparations are now on the market.

The chief advantages claimed for colloidal clay soap are that it absorbs dirt and grease, and removes them without any deleterious effect on the material, there being no injurious chemicals in the preparation, and that it is capable of removing unsaponifiable oily substances—a result which is not possible with the ordinary scouring media. It is stated to have a greater detergent power than ordinary soap and its antiseptic properties may be of considerable value.

It has been shown by Bancroft, the organic soaps depend partly on their solubility and decomposition (hydrolysis) for their detergent properties, and as such properties are not possessed by clay soap, they have a disadvantage in this respect.

As yet, the colloidal properties of clay have not been widely investigated in this direction, and a very large field may be opened out for the use of pure clays in soap manufacture, though the cost of purifying brick, tile and other clays—even though they are more plastic and contain more colloidal material—would, in most cases, be prohibitive.

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